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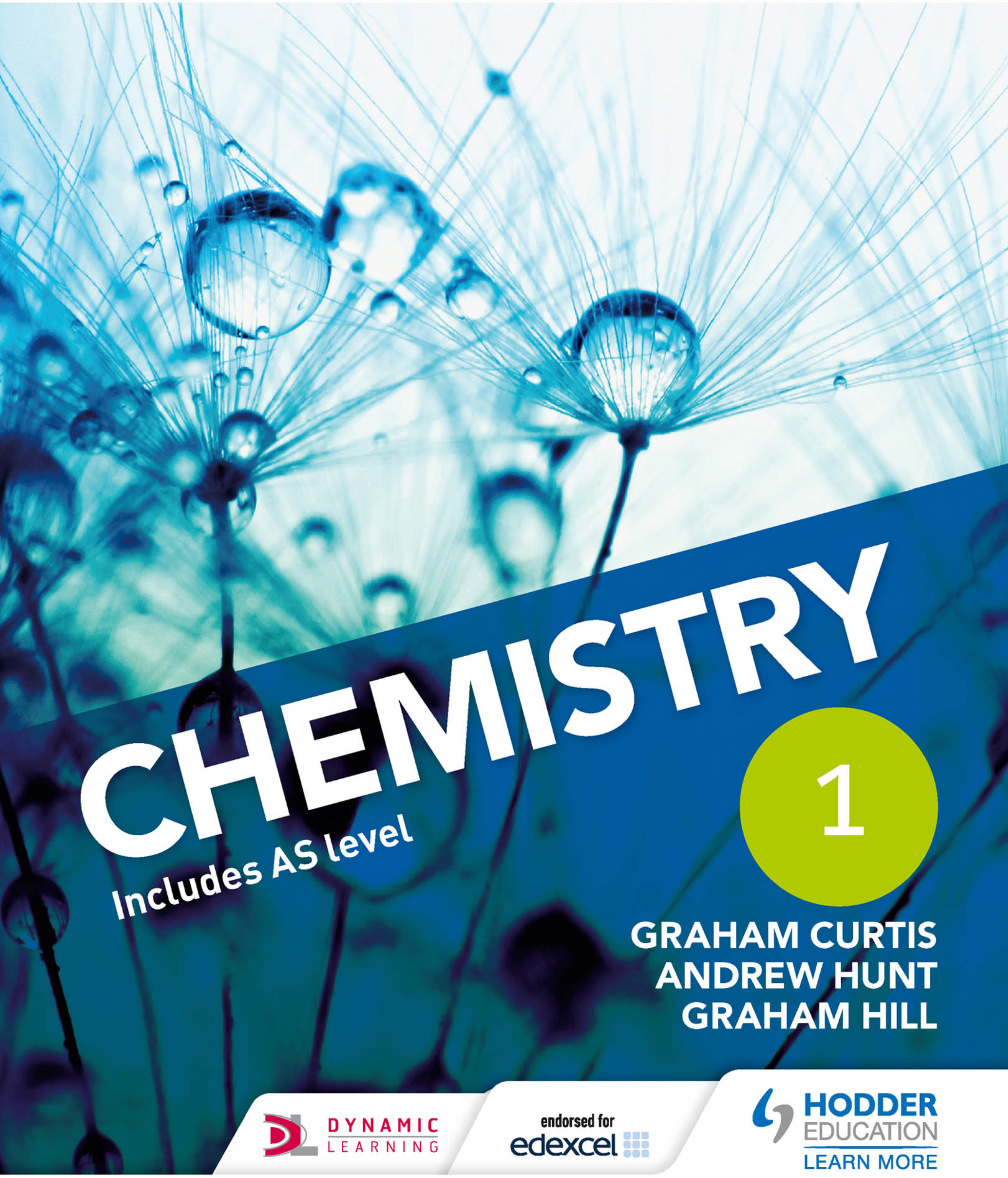

CHEMISTRY

1

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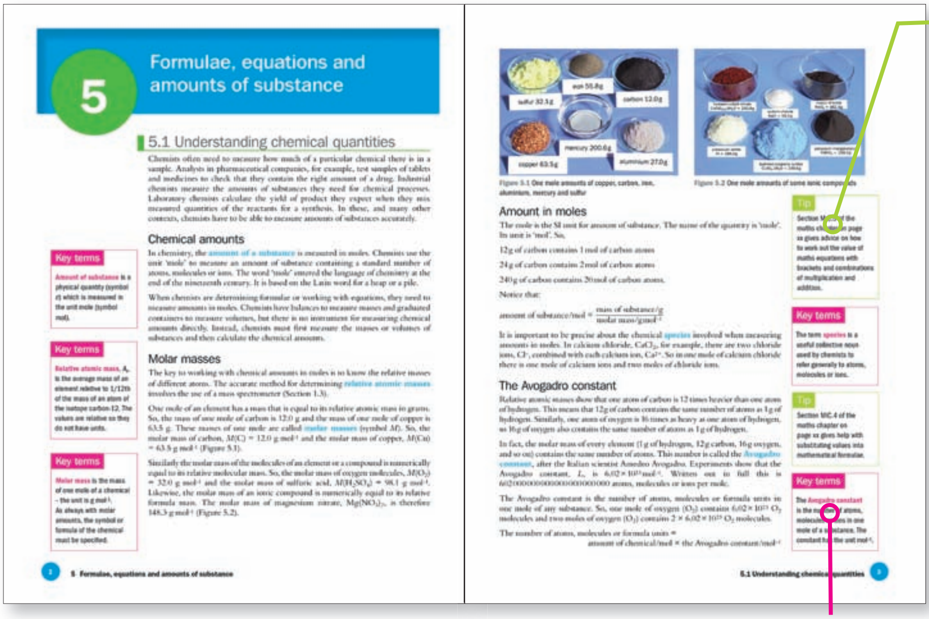
Get the most from this book

Welcome to the **Edexcel A level Chemistry 1 Student's Book**! This book covers Year 1 of the Edexcel A level Chemistry specification and all content for the Edexcel AS Chemistry specification.

The following features have been included to help you get the most from this book.



Tips

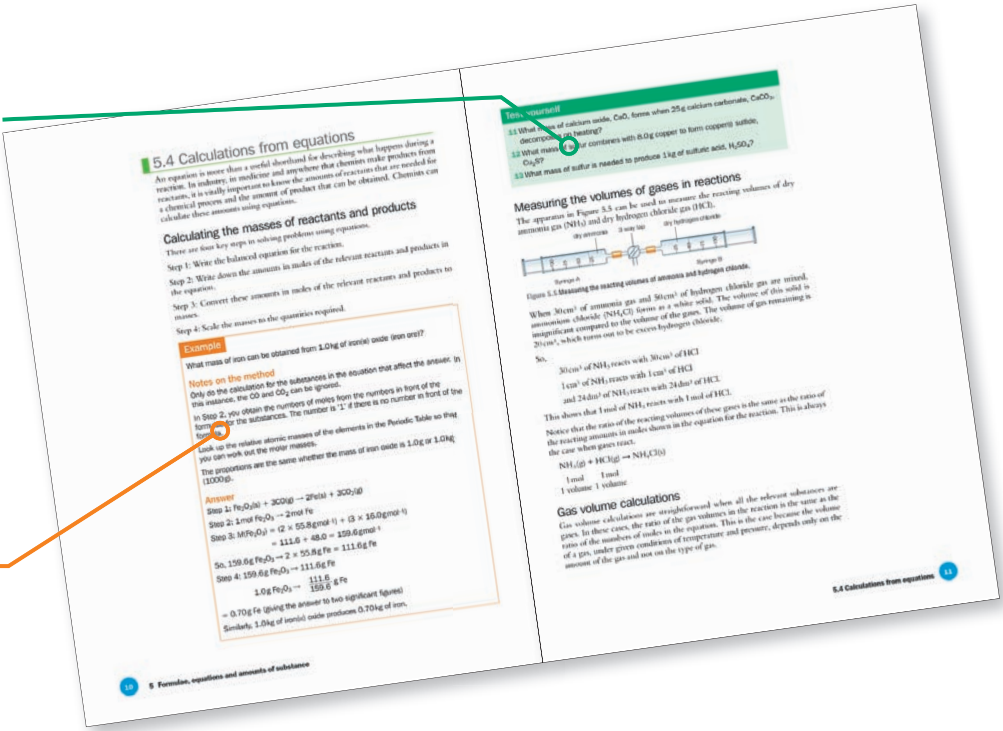
These highlight important facts, common misconceptions and signpost you towards other relevant topics.

Key terms and formulae

These are highlighted in the text and definitions are given in the margin to help you pick out and learn these important concepts.

Test yourself questions

These short questions, found throughout each chapter, are useful for checking your understanding as you progress through a topic.



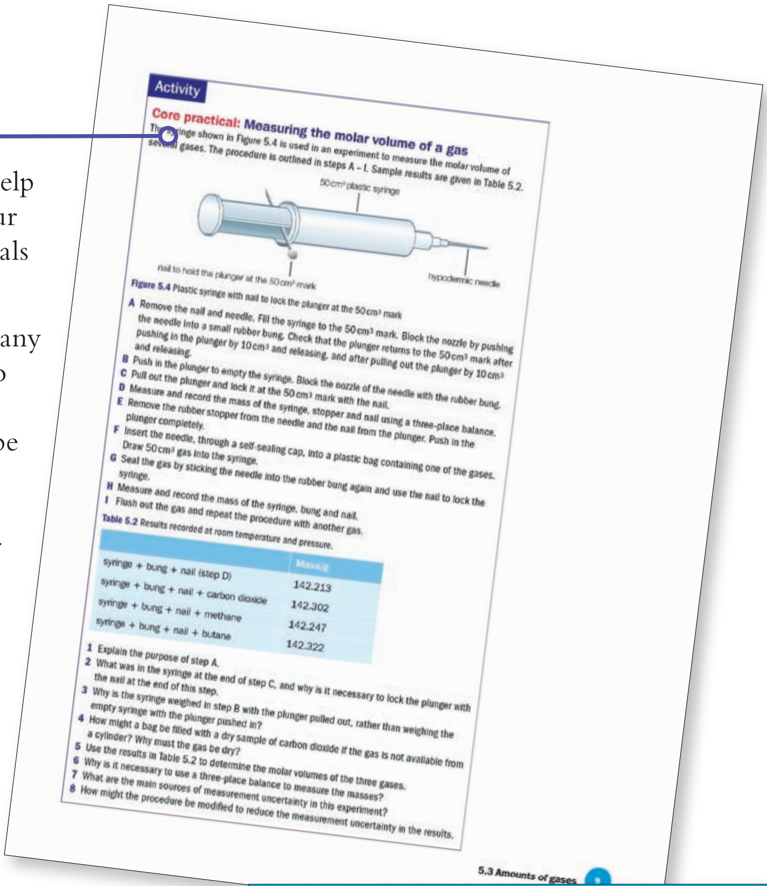
Examples

Examples of questions and calculations feature full workings and sample answers.

Activities and Core practicals

These practical-based activities will help consolidate your learning and test your practical skills. Edexcel's Core practicals are clearly highlighted.

In this edition the authors describe many important experimental procedures to conform to recent changes in the A level curriculum. Teachers should be aware that, although there is enough information to inform students of techniques and many observations for exam purposes, there is not enough information for teachers to replicate the experiments themselves, or with students, without recourse to CLEAPSS Hazcards or Laboratory worksheets which have undergone a risk assessment procedure.



Activity

Core practical: Measuring the molar volume of a gas

The syringe shown in Figure 5.4 is used in an experiment to measure the molar volume of several gases. The procedure is outlined in steps A – I. Sample results are given in Table 5.2.

Figure 5.4 Plastic syringe with nail to lock the plunger at the 50 cm³ mark

A Remove the nail and needle. Fill the syringe to the 50 cm³ mark. Block the nozzle by pushing the needle into a small rubber bung. Check that the plunger returns to the 50 cm³ mark after pushing in the plunger by 10 cm³ and releasing, and after pulling out the plunger by 10 cm³ and releasing.

B Push in the plunger to empty the syringe. Block the nozzle of the needle with the rubber bung.

C Pull out the plunger and lock it at the 50 cm³ mark with the nail.

D Measure and record the mass of the syringe, stopper and nail using a three-place balance.

E Remove the rubber stopper from the needle and the nail from the plunger. Push in the plunger completely.

F Insert the needle, through a self-sealing cap, into a plastic bag containing one of the gases. Draw 50 cm³ gas into the syringe.

G Seal the gas by sticking the needle into the rubber bung again and use the nail to lock the syringe.

H Measure and record the mass of the syringe, bung and nail.

I Flush out the gas and repeat the procedure with another gas.

Table 5.2 Results recorded at room temperature and pressure.

	Mass/g
syringe + bung + nail (step D)	142.213
syringe + bung + nail + carbon dioxide	142.302
syringe + bung + nail + methane	142.247
syringe + bung + nail + butane	142.322

1 Explain the purpose of step A.

2 What was in the syringe at the end of step C, and why is it necessary to lock the plunger with the nail at the end of this step.

3 Why is the syringe weighed in step B with the plunger pulled out, rather than weighing the empty syringe with the plunger pushed in?

4 How might a bag be filled with a dry sample of carbon dioxide if the gas is not available from a cylinder? Why must the gas be dry?

5 Use the results in Table 5.2 to determine the molar volumes of the three gases.

6 Why is it necessary to use a three-place balance to measure the masses?

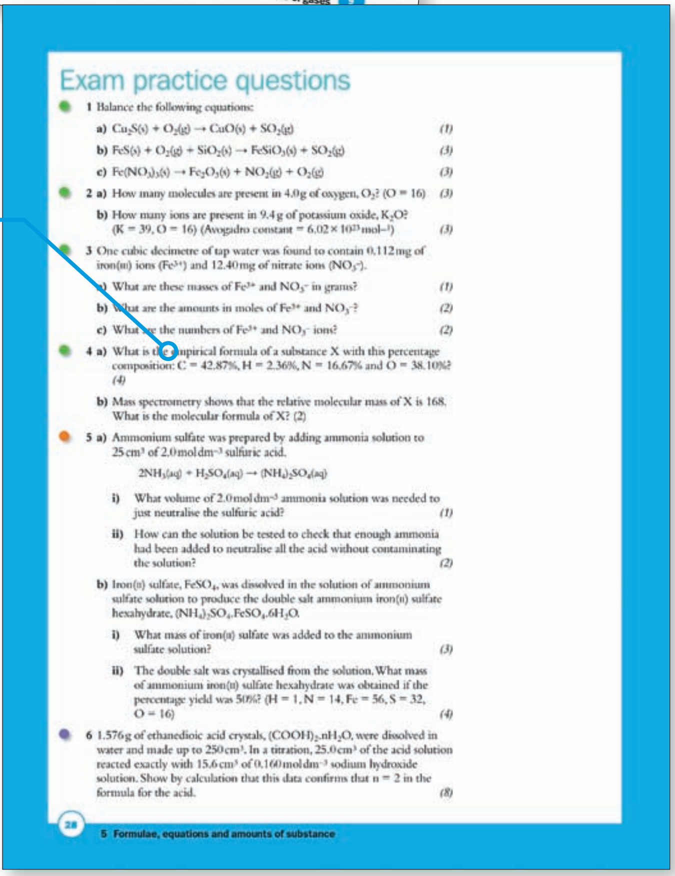
7 What are the main sources of measurement uncertainty in this experiment?

8 How might the procedure be modified to reduce the measurement uncertainty in the results.

5.3 Amounts of gases 9

Exam practice questions

You will find Exam practice questions at the end of every chapter. These follow the style of the different types of questions you might see in your examination and are colour coded to highlight the level of difficulty. Test your understanding even further with Maths questions and Stretch and challenge questions.



Exam practice questions

● 1 Balance the following equations:

a) $Cu_2S(s) + O_2(g) \rightarrow CuO(s) + SO_2(g)$ *(1)*

b) $FeS(s) + O_2(g) + SiO_2(s) \rightarrow FeSiO_3(s) + SO_2(g)$ *(3)*

c) $Fe(NO_3)_3(s) \rightarrow Fe_2O_3(s) + NO_2(g) + O_2(g)$ *(3)*

● 2 **a)** How many molecules are present in 4.0 g of oxygen, O_2? (O = 16) *(3)*

b) How many ions are present in 9.4 g of potassium oxide, K_2O? (K = 39, O = 16) (Avogadro constant = 6.02×10^{23} mol–1) *(3)*

● 3 One cubic decimetre of tap water was found to contain 0.112 mg of iron(III) ions (Fe^{3+}) and 12.40 mg of nitrate ions (NO_3^-).

a) What are these masses of Fe^{3+} and NO_3^- in grams? *(1)*

b) What are the amounts in moles of Fe^{3+} and NO_3^-? *(2)*

c) What are the numbers of Fe^{3+} and NO_3^- ions? *(2)*

● 4 **a)** What is the empirical formula of a substance X with this percentage composition: C = 42.87%, H = 2.36%, N = 16.67% and O = 38.10%? *(4)*

b) Mass spectrometry shows that the relative molecular mass of X is 168. What is the molecular formula of X? (2)

● 5 **a)** Ammonium sulfate was prepared by adding ammonia solution to 25 cm³ of 2.0 mol dm⁻³ sulfuric acid.

$$2NH_3(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

i) What volume of 2.0 mol dm⁻³ ammonia solution was needed to just neutralise the sulfuric acid? *(1)*

ii) How can the solution be tested to check that enough ammonia had been added to neutralise all the acid without contaminating the solution? *(2)*

b) Iron(II) sulfate, $FeSO_4$, was dissolved in the solution of ammonium sulfate solution to produce the double salt ammonium iron(II) sulfate hexahydrate, $(NH_4)_2SO_4.FeSO_4.6H_2O$.

i) What mass of iron(II) sulfate was added to the ammonium sulfate solution? *(3)*

ii) The double salt was crystallised from the solution. What mass of ammonium iron(II) sulfate hexahydrate was obtained if the percentage yield was 50%? (H = 1, N = 14, Fe = 56, S = 32, O = 16) *(4)*

● 6 1.576 g of ethanedioic acid crystals, $(COOH)_2.nH_2O$, were dissolved in water and made up to 250 cm³. In a titration, 25.0 cm³ of the acid solution reacted exactly with 15.6 cm³ of 0.160 mol dm⁻³ sodium hydroxide solution. Show by calculation that this data confirms that n = 2 in the formula for the acid. *(8)*

28 **5 Formulae, equations and amounts of substance**

Dedicated chapters for developing your **Maths** and **Preparing for your exam** are also included in this book.

Introduction

This book is an extensively revised, restructured and updated version of *Edexcel Chemistry for AS* by Graham Hill and Andrew Hunt. We have relied heavily on the contribution that Graham Hill made to the original book and are most grateful that he has encouraged us to build on his work. The team at Hodder Education, led initially by Hanneke Remsing and then by Emma Braithwaite, has made an extremely valuable contribution to the development of the book and the website resources. In particular, we would like to thank Abigail Woodman, the project manager, for her expert advice and encouragement. We are also grateful for the skilful work on the print and electronic resources by Anne Trevillion.

We have grouped each set of 'Exam practice' questions broadly by difficulty. In general, a question with 🟢 is straightforward and based directly on the information, ideas and methods described in the chapter. Each problem-solving part of the question typically only involves one step in the argument or calculation. A question with 🟠 is a more demanding, but still structured, question involving the application of ideas and methods to solve a problem with the help of data or information from this chapter or elsewhere. Arguments and calculations typically involve more than one step. The questions marked by 🟣 are hard and they may well expect you to bring together ideas from different areas of the subject. In these harder questions you may have to structure an argument or work out the steps required to solve a problem. In the earlier chapters, you may well decide not attempt the questions with 🟣 until you have gained wider experience and knowledge of the subject.

Practical work is of particular importance in A Level chemistry. Each of the Core Practicals in the specification features in the main chapters of this book with an outline of the procedure and data for you to analyse and interpret. Throughout the text there are references to Practical skills sheets which can be accessed via www.hoddereducation.co.uk/EdexcelAChemistry1. Sheets 1 to 3 provide general guidance, and the remainder provide more detailed guidance for the Core Practicals.

1. Practical skills for advanced chemistry
2. Assessing hazards and risks
3. Researching and referencing
4. Making measurements
5. Identifying errors and estimating uncertainties
6. Measuring chemical amounts by titration
7. Analysing inorganic unknowns
8. Synthesising organic liquids
9. Analysing organic unknowns
10. Measuring enthalpy changes

You will need to refer to the Edexcel Data booklet when answering some of the questions in this book. This will help you to become familiar with the booklet. This is important because you will need to use the booklet to find information when answering some questions in the examinations. You can download the Data booklet from the Edexcel website. It is part of the specification. The booklet includes the version of the periodic table that you use in the examinations.

Andrew Hunt and Graham Curtis

August 2014

Prior knowledge

1 Working like a chemist

Chemistry is about understanding the material world. Chemists develop their explanations by observing the properties of substances and looking at patterns of behaviour (Figure 1). They devise theories and models that can be used in chemical analysis and synthesis.

Figure 1 Aspirin is probably the commonest medicine in use. The bark of willow trees was used to ease pain for more than 2000 years. Early in the twentieth century, chemists extracted the active ingredient from willow bark. Their understanding of patterns in the behaviour of similar compounds enabled them to synthesise aspirin.

Tip

This first chapter surveys the main themes of chemistry and indicates how you will be learning more about chemistry during your A Level course. The chapters in this book build on what you already know about chemistry. The text and 'Test yourself' questions in the early part of each chapter can help you to check on what you have learned before and what you need to understand at the start of each topic.

Looking for patterns in chemical behaviour

Part of being a chemist involves getting a feel for the way in which chemicals behave. Chemists get to know chemicals just as people get to know their friends and family. They look for patterns in behaviour and recognise that some of the patterns are familiar. For example, the elements sodium and potassium are both soft and stored under oil because they react so readily with air and water; copper sulfate is blue, like other copper compounds. By understanding patterns, chemists can design and make plastics like polythene and medicines like aspirin.

Tip

The periodic table links together many of the key patterns of behaviour of elements. You will extend your knowledge of the periodic table in Chapter 1. You will also make a detailed study of patterns in the properties of the elements and compounds in some of the periodic table groups in Chapter 4.

Test yourself

Remind yourself of some patterns in the ways that chemicals behave.

1 What happens when a more reactive metal (such as zinc) is added to a solution in water of a compound of a less reactive metal (such as copper sulfate)?

2 What forms at the negative electrode (cathode) during the electrolysis of a solution of a salt?

3 What happens on adding an acid (such as hydrochloric acid) to a carbonate (such as calcium carbonate)?

4 What do sodium chloride, sodium bromide and sodium iodide look like?

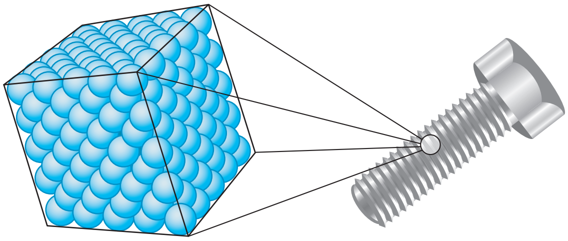
Tip

Theories of structure and bonding are key to understanding the properties of materials. You will extend your knowledge of these ideas when you study Chapter 2. Chapter 8 shows how measuring energy changes can provide evidence of the nature and strength of chemical bonds.

Discovering the composition and structure of materials

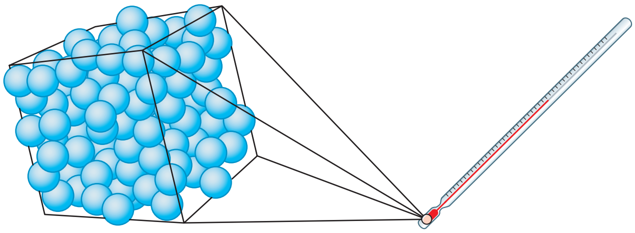
New materials exist only because chemists understand how atoms, ions and molecules are arranged in different materials, and about the forces which hold these particles together. Thanks to this knowledge, people can enjoy fibres that breathe but are waterproof, plastic ropes that are 20 times stronger than similar ropes of steel and metal alloys which can remember their shape.

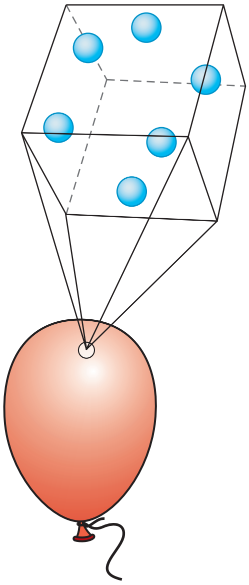
Understanding the structure and bonding of materials is a central theme in modern chemistry. Fundamental to this is an understanding of how the atoms, molecules or ions are arranged in different states of matter (Figure 2).



Particles in a solid are packed close together in a regular way. The particles do not move freely, but vibrate about fixed positions.

The particles in a liquid are closely packed but are free to move around, sliding past each other.





In a gas the particles are spread out, so the densities of gases are very low compared with solids and liquids. The particles move rapidly in a random manner, colliding with other particles and the walls of the container. Pressure is caused by particles hitting the walls. Lighter particles move faster than heavier ones.

Figure 2 The arrangements of particles in solids, liquids and gases.

Explaining and controlling chemical changes

Four key questions are at the heart of many chemical investigations.

- **How much?** – How much of the reactants is needed to make a product, how much of the product is produced, and how much energy is needed?
- **How fast?** – How can a reaction be controlled so that it goes at the right speed: not too fast and not too slow?
- **How far?** – Do the chemicals react completely, or does the reaction stop before all the reactants have turned into products? If it does, what can be done to get as big a yield as possible?
- **How do reactions occur?** – Which bonds between atoms break and which new bonds form during a reaction?

Tip

Chapters 5 and 8 show you how chemists answer the question 'How much?'. The questions 'How fast?' and 'How far?' are the focus of Chapters 9 and 10. Understanding how reactions occur is a feature of organic chemistry and so the study of reaction mechanisms is explored in the three parts of Chapter 6.

Developing new techniques and skills

Chemistry involves *doing* things as well as gaining knowledge and understanding about materials. Chemists use their thinking skills and practical skills to solve problems. One of the frontiers of today's chemistry involves nanotechnology, in which chemists work with particles as small as individual atoms (Figure 3).

Increasingly, chemists rely on modern instruments to explore structures and chemical changes. They also use information technology to store data, search for information and to publish their findings.

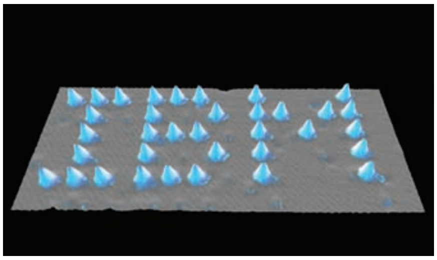


Figure 3 In the 1990s, two scientists working for IBM cooled a nickel surface to −269 °C in a vacuum chamber. Then they introduced a tiny amount of xenon so that some of the xenon atoms stuck to the nickel surface. Using a special instrument called a scanning tunnelling microscope, the scientists were able to move individual xenon atoms around on the nickel surface and construct the IBM logo. Each blue blob is the image of a single xenon atom.

Analysis and synthesis

A vital task for chemists is to analyse materials and find out what they are made of. When chemists have analysed a substance, they use symbols and formulae to show the elements it contains. Symbols are used to represent the atoms in elements; formulae are used to represent the ions and molecules in compounds.

Analysis is involved in checking that water is safe to drink and that food has not been contaminated. People may worry about pollution of the environment, but without chemical analysis they would not know about the causes or the scale of any pollution.

Chemists have devised many ingenious methods of analysis. Spectroscopy is especially important. At first spectroscopists just used visible light, but now they have found that they can find out much more by using other kinds of radiation such as ultraviolet and infrared rays, radiowaves and microwaves.

Chemistry is also about making things. Chemists take simple chemicals and join them together to make new substances. This is synthesis. On a large scale, the chemical industry converts raw materials from the earth, sea and air into valuable new products. A well-known example is the Haber process which uses natural gas and air to make ammonia. Ammonia is the chemical needed to make fertilisers, dyes and explosives. On a smaller scale, chemical reactions produce the specialist chemicals used for perfumes, dyes and medicines.

Tip

You will be developing your practical skills and understanding of practical chemistry during your A Level course. Most chapters in this book include activities and core practicals with results and data to analyse. General guidance on practical work can be accessed via the QR code for Chapter 1 on page 312.

Tip

Chapter 7 includes an account of some of the modern instrumental techniques used by chemists. Organic reactions that are important in synthesis feature in all parts of Chapter 6. The study of synthesis is a key feature of the organic chemistry in the second half of your A Level course.

Tip

Chemistry is a quantitative subject which involves a variety of types of calculation. You will find many worked examples in the chapters of this book that will help you to solve quantitative problems. The key mathematical ideas and techniques involved are described in Appendix A1.

Linking theories and experiments

Scientists test their theories by doing experiments. In chemistry, experiments often begin with careful observation of what happens as chemicals react and change. Theories are more likely to be accepted if predictions made from them turn out to be correct when tested by experiment.

One of the reasons why Mendeléev's periodic table was so successful was because he left gaps in his table for elements that had not yet been discovered and then made predictions about the properties of missing elements that turned out to be accurate (Table 1).

Table 1 Mendeléev's predictions for germanium in 1871 and the properties it was found to have after its discovery in 1886.

Mendeléev's predictions in 1871	Actual properties in 1886
Grey metal	Pale grey metal
Density 5.5 $g\,cm^{-3}$	Density 5.35 $g\,cm^{-3}$
Relative atomic mass 73.4	Relative atomic mass 72.6
Melting point 800 °C	Melting point 937 °C
Formula of oxide GeO_2	Ge forms GeO_2

Studying chemistry is more than about 'what we know'. It is also about 'how we know'. For example, the study of atomic structure has provided evidence about the nature and properties of electrons, and this has led to an explanation of the properties of elements and the patterns in the periodic table in terms of the electron structures of atoms.

2 Elements

Everything is made of elements. Elements are the simplest chemical substances which cannot be decomposed into simpler chemicals by heating or using electricity. There are over 100 elements, but from their studies of the stars, astronomers believe that about 90% of the Universe consists of just one element, hydrogen. Another 9% is accounted for by helium, leaving only 1% for all the other elements.

Metals and non-metals

Most of the elements, nearly 90 of them, are metals. It is usually easy to recognise a metal by its properties. Most metals are shiny, strong, bendable and good conductors of electricity (Figure 4).

There are only 22 non-metal elements: this includes a few which are solid at room temperature, such as carbon and sulfur, several gases, such as hydrogen, oxygen, nitrogen and chlorine, and just one liquid, bromine (Figure 5).

Figure 4 Samples of metals: from left to right, copper, zinc, lead and silver.

Figure 5 Samples of non-metals: sulfur, bromine, phosphorus (behind), carbon and iodine (in front).

Atoms of elements

Each element has its own kind of atom. An atom is the smallest particle of an element. Atoms consist of protons, neutrons and electrons. Every atom has a tiny nucleus surrounded by a cloud of electrons (Figure 6).

The mass of an atom is concentrated in the nucleus which consists of protons and neutrons. The protons are positively charged and the neutrons uncharged. All the atoms of a particular element have the same number of protons in the nucleus.

The electrons are negatively charged. The mass of an electron is so small that it can often be ignored. In an atom the number of electrons equals the number of protons in the nucleus. So the total negative charge equals the total positive charge and overall the atom is uncharged.

Tip

You will learn more about the properties of metal and non-metal elements in Chapter 4.

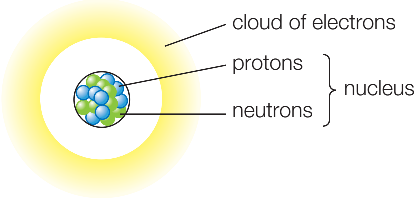


Figure 6 Diagram of an atom showing a nucleus surrounded by a cloud of electrons. This is not to scale. In reality the diameter of an atom is about 100 000 times bigger than the diameter of its nucleus.

Test yourself

5 Give examples of substances which can be split into elements by heating or by using an electric current (electrolysis).

6 Draw up a table to compare metal elements with non-metal elements using the following headings: Property; Metal; Non-metal.

Tip

You will learn more about atomic structure in Chapter 1.

3 Compounds

Compounds form when two or more elements combine. Apart from the atoms of the elements helium and neon, all elements can combine with other elements.

In order to explain the properties of compounds, chemists need to find out how the atoms, molecules or ions are arranged (the structure) and what holds them together (the bonding).

Compounds of non-metals with non-metals

Water, carbon dioxide, methane in natural gas, sugar and ethanol ('alcohol') are examples of compounds of two or more non-metals. These compounds of non-metals have molecular structures.

The covalent bonds between the atoms in molecules are strong but the attractive forces between molecules are weak. This means that molecular compounds melt and vaporise easily. They may be gases, liquids or solids at room temperature and they do not conduct electricity.

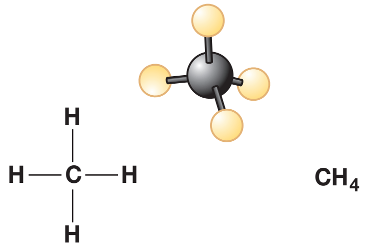


Figure 7 Ways of representing a molecule of methane.

Methane contains one carbon atom bonded to four hydrogen atoms. The formula of the molecule is CH_4. Figure 7 shows three ways of representing a methane molecule.

Chemists have to analyse compounds to find their formulae. The results of analysis give an empirical (experimental) formula. This shows the simplest whole number ratio of the atoms of different elements in a compound, for example CH_4 for methane and CH_3 for ethane.

Tip

You will learn more about how chemists determine the formulae of compounds in Sections 5.2 and 5.3.

More information is needed to work out the molecular formula of a compound showing the numbers of atoms of the different elements in one molecule of the compound. For example, CH_4 is the molecular formula of methane but C_2H_6 is the molecular formula of ethane.

It is often possible to write the formula of non-metal compounds given how many covalent bonds the atoms normally form (Table 2).

Table 2 Symbols, number of bonds and colour codes of some non-metals.

Element	Symbol	Number of bonds formed	Colour in molecular models
Carbon	C	4	Black
Nitrogen	N	3	Blue
Oxygen	O	2	Red
Sulfur	S	2	Yellow
Hydrogen	H	1	White
Chlorine	Cl	1	Green

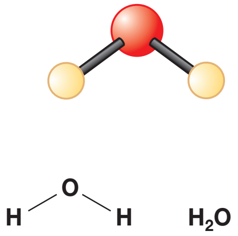


Figure 8 Ways of representing a molecule of water.

Water is a compound of oxygen and hydrogen. Oxygen atoms form two bonds and hydrogen atoms form one bond. So two hydrogen atoms can bond to one oxygen atom (Figure 8) and the formula of water is H_2O.

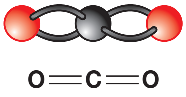


Figure 9 Bonding in carbon dioxide showing the double bonds between atoms.

There are double and even triple bonds between the atoms in some non-metal compounds (Figure 9). Notice also that there is a colour code for the atoms of different elements in molecular models – these colours are shown in Table 2.

In practice, it is not possible to predict the formulae of all non-metal compounds. For example, the simplified bonding rules in Table 2 cannot account for the formulae of carbon monoxide, CO, sulfur dioxide, SO_2, or sulfur hexafluoride, SF_6.

Figure 10 Quartz crystal from Sentis, Switzerland. Quartz is one of the commonest minerals of the Earth's crust. It consists of silicon dioxide, SiO_2.

There are some compounds made up of non-metal elements in which the covalent bonding links all the atoms in a crystal together in a giant lattice. Silicon dioxide, SiO_2, is an important example which is found in many igneous rocks (Figure 10). Compounds with covalent giant structures are hard and melt at high temperatures.

Test yourself

7 Draw the various ways of representing the following molecular compounds in the style of Figure 7:

a) hydrogen chloride **b)** carbon disulfide.

8 Name the elements present and work out the formula of the following molecular compounds:

a) hydrogen sulfide **b)** dichlorine oxide

c) ammonia (hydrogen nitride).

Tip

You will learn more about the bonding in compounds of non-metals with non-metals in Chapter 2.

Compounds of metals with non-metals

Common salt (sodium chloride), limestone (calcium carbonate) and copper sulfate are all examples of compounds of metals with non-metals. These metal/non-metal compounds consist of a giant structure of ions. An ion is an atom, or a group of atoms, which has become electrically charged by the loss or gain of one or more electrons. Generally metal atoms form positive ions by losing electrons while non-metal atoms form negative ions by gaining electrons. For example, sodium chloride consists of positive sodium ions, Na^+, and negative chloride ions, Cl^- (Figure 11).

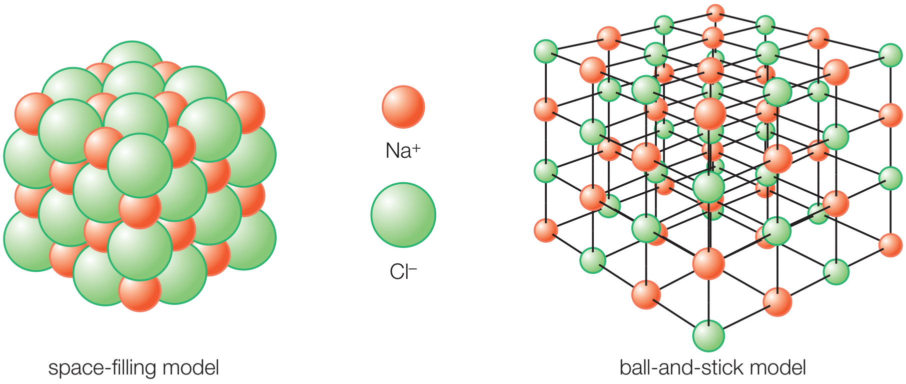


Figure 11 A space-filling model and a ball-and-stick model showing the giant structure of sodium chloride.

The strong ionic bonding between the ions means that such compounds melt at much higher temperatures than the molecular compounds of non-metals. They are solids at room temperature. They conduct electricity as molten liquids but not as solids. Metal/non-metal compounds conduct electricity when heated above their melting points because the ions are free to move in the liquid state.

The formula of sodium chloride is NaCl because the positive charge on one Na^+ ion is balanced by the negative charge on one Cl^- ion. In a crystal of sodium chloride there are equal numbers of sodium ions and chloride ions.

The formulae of all metal/non-metal (ionic) compounds can be worked out by balancing the charges on positive and negative ions. For example, the formula of potassium oxide is K_2O. Here, two K^+ ions balance the charge on one O^{2-} ion.

Elements such as iron, which have two different ions (Fe^{2+} and Fe^{3+}), have two sets of compounds – iron(II) compounds such as iron(II) chloride, $FeCl_2$, and iron(III) compounds such as iron(III) chloride, $FeCl_3$.

Table 3 The names and formulae of some ionic compounds.

Name of compound	Ions present	Formula
Magnesium nitrate	Mg^{2+} and NO_3^-	$Mg(NO_3)_2$
Aluminium hydroxide	Al^{3+} and OH^-	$Al(OH)_3$
Zinc bromide	Zn^{2+} and Br^-	$ZnBr_2$
Lead(II) nitrate	Pb^{2+} and NO_3^-	$Pb(NO_3)_2$
Calcium iodide	Ca^{2+} and I^-	CaI_2
Copper(II) carbonate	Cu^{2+} and CO_3^{2-}	$CuCO_3$
Silver sulfate	Ag^+ and SO_4^{2-}	Ag_2SO_4

Table 3 shows the names and formulae of some ionic compounds. Notice that the formula of magnesium nitrate is $Mg(NO_3)_2$. The brackets round NO_3^- show that it is a single unit containing one nitrogen and three oxygen atoms bonded together with a 1− charge. Other ions, such as OH^-, SO_4^{2-} and CO_3^{2-}, must also be treated as single units and put in brackets when there are two or three of them in a formula.

Tip

You will learn more about ionic crystals and ionic bonding in Chapter 2.

Test yourself

9 This question concerns the substances ice, salt, sugar, copper, steel and limestone.

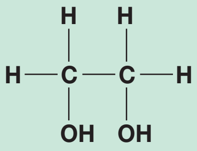
Which of these substances contain:

a) uncombined atoms

b) ions

c) molecules?

10 The structure of the main constituent in antifreeze is:



What is:

a) its molecular formula

b) its empirical formula?

11 The formula of aluminium hydroxide must be written as $Al(OH)_3$. Why is $AlOH_3$ wrong?

12 Write the formulae of the following ionic compounds given these charges on ions: Al^{3+}, Fe^{2+}, Fe^{3+}, K^+, Pb^{2+}, Zn^{2+}, CO_3^{2-}, O^{2-}, OH^-, SO_4^{2-}:

a) potassium sulfate

b) aluminium oxide

c) lead carbonate

d) zinc hydroxide

e) iron(III) sulfate.

13 Which of the following compounds consist of molecules and which consist of ions?

- **a)** octane (C_8H_{18}) in petrol
- **b)** copper(I) oxide
- **c)** concentrated sulfuric acid
- **d)** lithium fluoride
- **e)** phosphorus trichloride

14 Compare non-metal (molecular) compounds with metal/non-metal (ionic) compounds in:

- **a)** melting temperatures and boiling temperatures
- **b)** conduction of electricity as liquids.

4 Chemical changes

Burning, rusting and fermentation are all examples of chemical reactions. Under the right conditions, chemical bonds break and new ones form. This is what happens during a chemical reaction to create new chemicals.

Figure 12 shows a simple way of demonstrating that when hydrogen burns the product is water. Hydrogen and oxygen (in the air) are both gases at room temperature. When the gases react the changes give out so much energy that there is a flame. Water condenses on cooling the steam that forms in the flame.

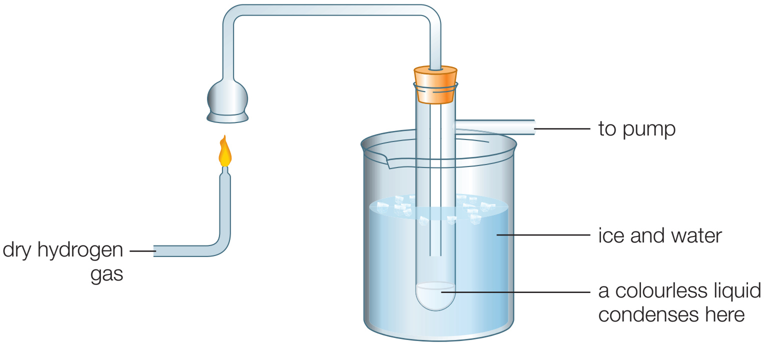


Figure 12 Demonstration that burning hydrogen produces water.

One way of describing what happens during a reaction is to write a word equation. Writing word equations identifies the reactants (on the left) and products (on the right), so it is a useful first step towards a balanced equation with symbols.

When hydrogen burns:

$$\underbrace{\text{hydrogen(g)} + \text{oxygen(g)}}_{\text{reactants}} \rightarrow \underbrace{\text{water(l)}}_{\text{product}}$$

When they are looking at this change, chemists imagine what is happening to the molecules. The trick is to interpret the visible changes in terms of theories about atoms and bonding. Models help to make the connection.

The hydrogen molecules and oxygen molecules consist of pairs of atoms. They are diatomic molecules. Figure 13 shows how molecular models give a picture of the reaction at an atomic level.

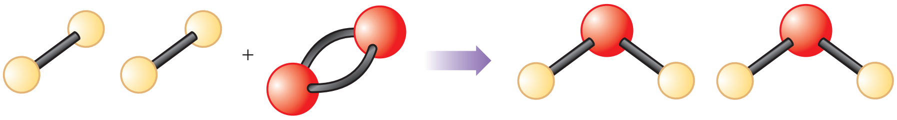


Figure 13 Model equation to show hydrogen reacting with oxygen.

The formula of water is H_2O. Each water molecule contains only one oxygen atom. So one oxygen molecule can give rise to two water molecules, provided that there are two hydrogen molecules available to supply all the hydrogen atoms necessary.

There is the same number of atoms on both sides of the equation. The atoms have simply been rearranged.

Chemists normally use symbols rather than models to describe reactions. Symbols are much easier to write or type. State symbols added to a symbol equation show whether the substances are solid, liquid, gases or dissolved in water.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Modelling is increasingly important in modern chemistry but now the modelling is usually carried out with computers. In 2013 the Nobel prize for chemistry was awarded to Martin Karplus, Michael Levitt and Arieh Warshel whose work, in the 1970s, laid the foundation for the powerful computer modelling programs that are used to understand and predict chemical processes.

Tip

You will learn more about writing equations for chemical reactions in Sections 3.2 and 4.1.

Test yourself

15 a) Write a balanced symbol equation for the reaction of methane, CH_4, with oxygen.

b) Draw a diagram, similar to that shown in Figure 13, to show what happens when methane burns in oxygen.

16 Write balanced equations, with state symbols, for the following word equations:

a) hydrogen + chlorine → hydrogen chloride

b) zinc + hydrochloric acid (HCl) → zinc chloride + hydrogen

c) ethane + oxygen → carbon dioxide + water

d) iron + chlorine → iron(III) chloride.

5 Acids, bases, alkalis and salts

Acids

Pure acids may be solids (such as citric, Figure 14, and tartaric acids), liquids (such as sulfuric, nitric and ethanoic acids) or gases (such as hydrogen chloride which becomes hydrochloric acid when it dissolves in water). All these acids are compounds with characteristic properties:

- they form solutions in water with a pH below 7
- they change the colour of indicators such as litmus
- they react with metals above hydrogen in the reactivity series forming hydrogen plus an ionic metal compound called a salt

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$$

Figure 14 Crystals of the solid acid citric acid. This acid was first obtained as a pure compound in 1784 when it was crystallised from lemon juice.

- they react with metal oxides and metal hydroxides to form salts and water

  $CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$

- they react with carbonates to form salts, carbon dioxide and water

  $ZnCO_3(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + CO_2(g) + H_2O(l)$

Bases and alkalis

Bases are 'anti-acids'. They are the chemical opposites of acids. Alkalis are bases which dissolve in water. The common laboratory alkalis are sodium hydroxide, potassium hydroxide, calcium hydroxide and ammonia. Alkalis form solutions with a pH above 7, so they change the colours of acid–base indicators. Alkalis are useful because they neutralise acids.

Manufacturers produce powerful oven and drain cleaners containing sodium hydroxide or potassium hydroxide because they can break down and remove greasy dirt. These strong alkalis are highly 'caustic'. They attack skin, producing a chemical burn. Even dilute solutions of these alkalis can be hazardous, especially if they get into your eyes (Section 4.3).

Test yourself

17 Write full balanced equations for the reactions of hydrochloric acid with:

a) zinc

b) calcium oxide

c) potassium hydroxide

d) nickel(II) carbonate.

Salts

Salts are ionic compounds formed when an acid reacts with a base. In the formula of a salt, the hydrogen of an acid is replaced by a metal ion. For example, magnesium sulfate, $MgSO_4$, is a salt of sulfuric acid, H_2SO_4.

Salts can be regarded as having two 'parents'. They are related to a parent acid and to a parent base. Hydrochloric acid, for example, gives rise to the salts called chlorides, such as sodium chloride, calcium chloride and ammonium chloride. The base sodium hydroxide gives rise to sodium salts, such as sodium chloride, sodium sulfate and sodium nitrate.

Neutralisation is not the only way to make a salt. Some metal chlorides, for example, are made by heating metals in a stream of chlorine. This is useful for making anhydrous chlorides, such as aluminium chloride.

Test yourself

18 Name the salts formed from these pairs of acids and bases:

a) nitric acid and potassium hydroxide

b) hydrochloric acid and calcium hydroxide

c) sulfuric acid and copper(II) oxide

d) ethanoic acid and sodium hydroxide.

1 Atomic structure and the periodic table

1.1 Models of atomic structure

Early ideas about atoms

The idea that all substances are made of atoms is a very old one. It was suggested by Greek philosophers, including Democritus, more than 2400 years ago (Figure 1.1).

Figure 1.1 The Greek philosopher Democritus, who lived from 460 to 370 BCE.

Democritus was a philosopher whose idea was that if a lump of metal, such as iron, was cut into smaller and smaller pieces, the end result would be miniscule and invisible particles that could not be cut any smaller. Democritus called these smallest particles of matter 'atomos' meaning 'indivisible'. He explained the properties of materials such as iron in terms of the shapes of the atoms and the 'hooks' that he imagined joined them together.

Democritus was a great thinker but he did not do experiments and he had no way to test his ideas. He, and other atomists of his time, failed to convince everybody that the theory was correct. There were other competing theories and no convincing reasons to accept the idea of atoms in preference to other ideas.

Modern atomic theory grew from work started about 2000 years after Democritus, when scientists in Europe started to purify substances and to carry out experiments with them. They found that many substances could be broken down (decomposed) into simpler substances, which they called elements. These elements could then be combined to make new compounds.

In the eighteenth century, chemists began to make accurate measurements of the quantities of substances involved in reactions. To their surprise, they found that the weights of elements which reacted were always in the same proportions. So, for example, water always contained 1 part by weight of hydrogen to 8 parts by weight of oxygen. And, black copper oxide always contained 1 part by weight of oxygen to 4 parts by weight of copper.

Figure 1.2 John Dalton was born in 1766 in the village of Eaglesfield in Cumbria. His father was a weaver. Dalton was always curious and liked to study. When he was only 12 years old, he started to teach children in the village school. For most of his life, he taught science and carried out experiments at the Presbyterian College in Manchester.

At the start of the nineteenth century, John Dalton puzzled over these results. He concluded that if elements were made of indivisible particles, then everything made sense (Figure 1.2). Compounds, like copper oxide, were made of particles of copper and oxygen with different masses and these always combined in the same ratios. Dalton called the indivisible particles atoms in recognition of the ideas first proposed by Democritus.

Dalton began to publish his atomic theory in 1808. The main points in his theory were that:

- all elements are made up of indivisible particles called atoms
- all the atoms of a given element are identical and have the same mass

- the atoms of different elements have different masses
- atoms can combine to form molecules in compounds
- all the molecules of a given compound are identical.

Although some scientists were reluctant to accept Dalton's ideas, his atomic theory caught on because it could explain the results of many experiments.

Even today, Dalton's atomic theory is still useful and very helpful. However, research has since shown that atoms are not indivisible and that all atoms of the same element are not identical.

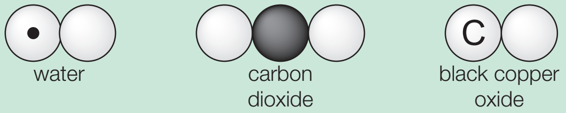
Test yourself

1 Look at the five main points in Dalton's atomic theory. Which of these points:

a) are still correct

b) are now incorrect?

2 Look at the formulae below which Dalton used for water, carbon dioxide and black copper oxide.



a) Write the formulae that are used today for these compounds.

b) What symbols did Dalton use for carbon, oxygen, hydrogen and copper?

c) Which one of the formulae did Dalton get wrong?

Inside atoms

For much of the nineteenth century, scientists continued with the idea that atoms were just as Dalton had described them: solid, indestructible particles similar to tiny snooker balls. Then, between 1897 and 1932, scientists carried out several series of experiments that revealed that atoms contain three smaller particles: electrons, protons and neutrons.

The discovery of electrons

In 1897, J.J. Thomson was investigating the conduction of electricity by gases in his laboratory at Cambridge. When he connected 15 000 volts across the terminals of a tube containing air, the glass walls glowed bright green. Rays travelling in straight lines from the negative terminal hit the glass and made it glow. Experiments showed that a narrow beam of the rays could be deflected by an electric field (Figure 1.3). When passed between charged plates, the rays always bent towards the positive plate. This showed they were negatively charged.

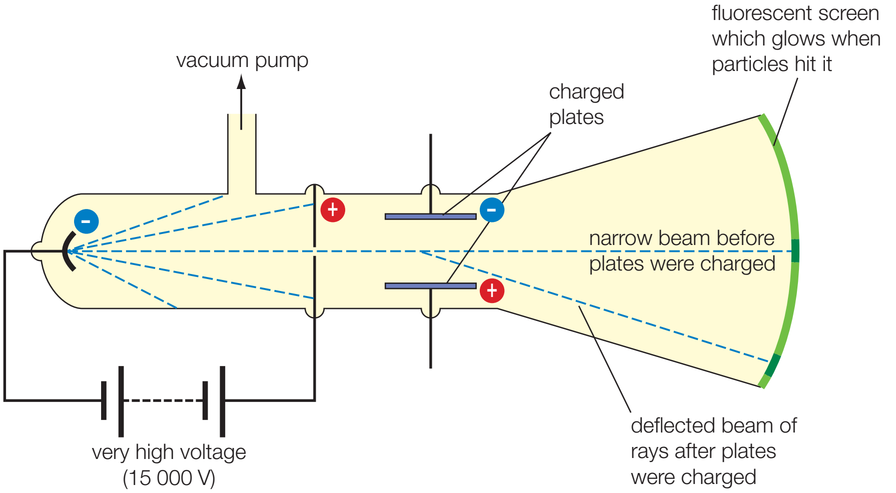

vacuum pump
fluorescent screen which glows when particles hit it
charged plates
narrow beam before plates were charged
very high voltage (15 000 V)
deflected beam of rays after plates were charged
+
−

Figure 1.3 The effect of charged plates on a beam of electrons.

Further study showed that the rays consisted of tiny negative particles about 2000 times lighter than hydrogen atoms. This surprised Thomson. He had discovered particles smaller than atoms. Thomson called the tiny negative particles electrons.

Thomson obtained the same electrons with different gases in the tube and when the terminals were made of different substances. This suggested to him that the atoms of all substances contain electrons. Thomson knew that atoms had no electrical charge overall. So, the rest of the atom must have a positive charge to balance the negative charge of the electrons.

In 1904, Thomson published his model for the structure of atoms. He suggested that atoms were tiny balls of positive material with electrons embedded in it like fruit in a Christmas pudding. As a result, Thomson's idea became known as the 'plum pudding' model of atomic structure (Figure 1.4).

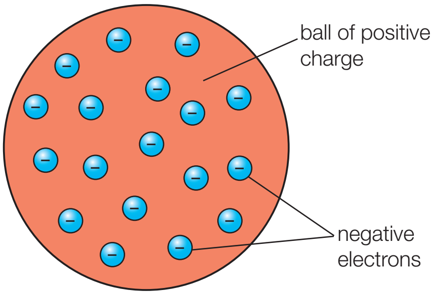

ball of positive charge
negative electrons

Figure 1.4 Thomson's plum pudding model for the structure of atoms.

Rutherford and the nuclear atom

Radioactivity was discovered by Henri Becquerel in Paris in 1896. Two years later, Ernest Rutherford, in Manchester, showed that there were at least two types of radiation given out by radioactive materials. He called these alpha rays and beta rays.

At the time, Rutherford and his colleagues didn't know exactly what alpha rays were. But they did know that alpha rays contained particles. These alpha particles were small, heavy and positively charged. Rutherford and his colleagues realised that they could use the alpha particles as tiny 'bullets' to fire at atoms.

In 1909, two of Rutherford's colleagues, Hans Geiger and Ernest Marsden, directed narrow beams of positive alpha particles at very thin gold foil only a few atoms thick (Figure 1.5). They expected the particles to pass straight through the foil or to be deflected slightly.

The results showed that:

- most of the alpha particles went straight through the foil
- some of the alpha particles were scattered (deflected) by the foil
- a few alpha particles rebounded from the foil.

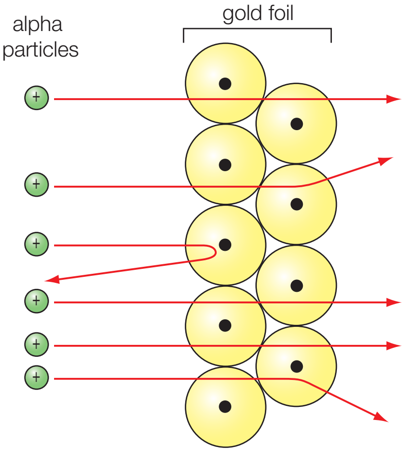

alpha particles
gold foil

Figure 1.5 When positive alpha particles are directed at a very thin sheet of gold foil, they emerge at different angles. Most pass straight through the foil, some are deflected and a few appear to rebound from the foil.

Test yourself

3 Suggest explanations for these results of the Geiger–Marsden experiment:

a) Most of the alpha particles passed straight through the foil.

b) Some alpha particles were deflected.

c) A few alpha particles rebounded from the foil.

4 a) What did the Geiger–Marsden experiment suggest about the size of any positive and negative particles in the gold atoms.

b) Why did the results cast doubts on Thomson's plum pudding model for atomic structure?

5 Rutherford and his team published a series of papers about their work, including a paper *The Laws of Deflexion of α Particles through Large Angles* in a 1913 edition the *Philosophical Magazine.* Why is it important that scientists publish their experimental results and theories?

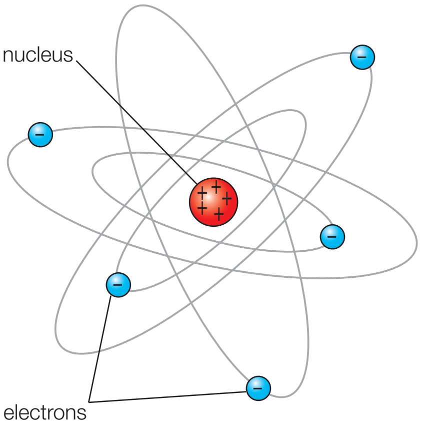


Figure 1.6 Rutherford's nuclear model for the structure of atoms. Rutherford pictured atoms as miniature solar systems with electrons orbiting the nucleus like planets around the Sun.

Rutherford came up with a new model of the atom to explain the results of Geiger and Marsden's experiment. In this model a very small positive nucleus is surrounded by a much larger region of empty space in which electrons orbit the nucleus like planets orbiting the Sun (Figure 1.6).

Rutherford's nuclear model quickly replaced Thomson's plum pudding model and it is still the basis of models of atomic structure used today.

The work of Thomson, Rutherford and their colleagues showed that:

- atoms have a small positive nucleus surrounded by a much larger region of empty space in which there are tiny negative electrons (Figure 1.7)
- the positive charge of the nucleus is due to positive particles which Rutherford called protons
- protons are about 2000 times heavier than electrons
- the positive charge on one proton is equal in size, but opposite in sign, to the negative charge on one electron
- atoms have equal numbers of protons and electrons, so the positive charges on the protons cancel the negative charges on the electrons
- the smallest atoms are those of hydrogen with one proton and one electron. The next smallest atoms are those of helium with two protons and two electrons, then lithium atoms with three protons and three electrons, and so on.

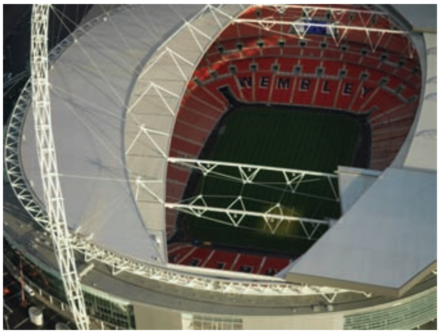


Figure 1.7 If the nucleus of a hydrogen atom were to be enlarged to the size of a marble and put in the centre of the Wembley pitch, the atom's one electron would be whizzing around somewhere in the stands.

Chadwick and the discovery of neutrons

Although Rutherford was successful in explaining many aspects of atomic structure, one big problem remained. If hydrogen atoms contain one proton and helium atoms contain two protons, then the relative masses of hydrogen and helium atoms should be one and two, respectively. But the mass of helium atoms relative to hydrogen atoms is four and not two. It took the discovery of isotopes and much further research before the problem was solved.

In 1932, James Chadwick, in Cambridge, solved the mystery of the extra mass in helium atoms. Chadwick studied the effects of bombarding a beryllium target with alpha particles. This produced a new kind of radiation with no electric charge but with enough energy to release protons when fired at a material such as wax. In time, Chadwick was able to demonstrate that there must be uncharged particles in the nuclei of atoms, as well as positively charged protons. Chadwick called these particles neutrons. It was soon found that neutrons had the same mass as protons.

The discovery of neutrons accounted for the relative masses of hydrogen and helium atoms. Hydrogen atoms have one proton and no neutrons, so a hydrogen atom has a relative mass of one unit, Helium atoms have two protons and two neutrons, so a helium atom has a relative mass of four units. This makes a helium atom four times as heavy as a hydrogen atom.

It is now understood that all atoms are made up from protons, neutrons and electrons. The relative masses, relative charges and positions within atoms of these sub-atomic particles are summarised in Table 1.1.

Tip

For a time, protons, neutrons and electrons were described as ‘fundamental’ or ‘elementary’ particles – that is particles not made up of anything smaller or simple. Electrons are still thought to be fundamental particles but protons and electrons are now known to be made up of quarks.

Table 1.1 Relative masses, relative charges and positions in atoms of protons, neutrons and electrons.

Particle	Mass relative to that of a proton	Charge relative to that on a proton	Position in the atom
Proton	1	+1	Nucleus
Neutron	1	0	Nucleus
Electron	$\frac{1}{1840}$	−1	Shells

Test yourself

6 Draw and label a diagram to show how Chadwick explained that the mass of a helium atom is four times the mass of a hydrogen atom.

7 Summarise the development of atomic models in a table with the models listed in the left-hand column and a brief note on the evidence which gave rise to the models in the right-hand column.

1.2 Atomic number and mass number

All the atoms of a particular element have the same number of protons, and atoms of different elements have different numbers of protons.

Hydrogen atoms are the simplest of all atoms – they have just one proton and one electron. The next simplest are atoms of helium with two protons and two electrons, then lithium with three protons, and so on. Large atoms have large numbers of protons and electrons. For example, gold atoms (Figure 1.8) have 79 protons and 79 electrons.

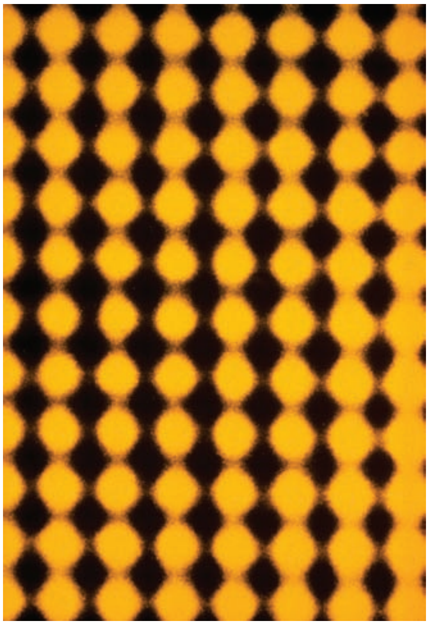


Figure 1.8 Photo of the surface of a gold crystal taken through an electron microscope. Each yellow blob is a separate gold atom – the atoms have been magnified about 35 million times.

The only atoms with one proton are those of hydrogen; the only atoms with two protons are those of helium; the only atoms with three protons are those of lithium, and so on. This means that the number of protons in an atom decides which element it is. Because of this, scientists have a special name for the number of protons in the nucleus of an atom. They call it the

atomic number and use the symbol Z to represent it. So, hydrogen has an atomic number of 1 ($Z = 1$), helium has an atomic number of 2 ($Z = 2$), and so on.

Protons do not account for all the mass of an atom – neutrons in the nucleus also contribute. Therefore, the mass of an atom depends on the number of protons plus neutrons. This number is called the **mass number** of the atom (symbol A).

Hydrogen atoms, with one proton and no neutrons, have a mass number of 1. Lithium atoms, with 3 protons and 4 neutrons, have a mass number of 7 and aluminium atoms, with 13 protons and 14 neutrons, have a mass number of 27.

There is an agreed shorthand for showing the mass number and atomic number of an atom. This is shown for a potassium atom, $^{39}_{19}\mathrm{K}$, in Figure 1.9. Ions can also be represented using this shorthand. For example, the potassium ion can be written as $^{39}_{19}\mathrm{K}^+$.

Key terms

The **atomic number** of an atom is the number of protons in its nucleus. The term 'proton number' is sometimes used for atomic number.

The **mass number** of an atom is the number of protons plus neutrons in its nucleus. Protons and neutrons are sometimes called nucleons, so the term 'nucleon number' is an alternative to mass number.

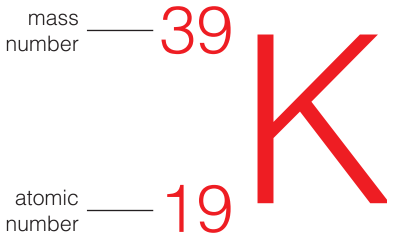


Figure 1.9 The mass number and atomic number can be shown with the symbol of an atom.

Test yourself

8 Use Figure 1.8, and the information in the caption, to estimate the diameter of a gold atom in nanometres.

9 How many protons, neutrons and electrons are there in the following atoms and ions:

- **a)** $^{9}_{4}\mathrm{Be}$
- **b)** $^{39}_{19}\mathrm{K}$
- **c)** $^{235}_{92}\mathrm{U}$
- **d)** $^{19}_{9}\mathrm{F}^-$
- **e)** $^{40}_{20}\mathrm{Ca}^{2+}$?

10 Write symbols showing the mass number and atomic number for these atoms and ions:

- **a)** an atom of oxygen with 8 protons, 8 neutrons and 8 electrons
- **b)** an atom of argon with 18 protons, 22 neutrons and 18 electrons
- **c)** an ion of sodium with a 1+ charge and a nucleus of 11 protons and 12 neutrons
- **d)** an ion of sulfur with a 2– charge and a nucleus with 16 protons and 16 neutrons.

1.3 Comparing the masses of atoms – mass spectrometry

Individual atoms are far too small to be weighed, but in 1919 F.W. Aston invented the mass spectrometer. This gave scientists an accurate method of comparing the relative masses of atoms and molecules. Since its invention, mass spectrometry has been developed into a sophisticated technique for chemical analysis based on a variety of types of instrumentation.

A mass spectrometer separates atoms and molecules according to their mass, and also shows the relative numbers of the different atoms and molecules present. Figure 1.10 shows a schematic diagram of a mass spectrometer.

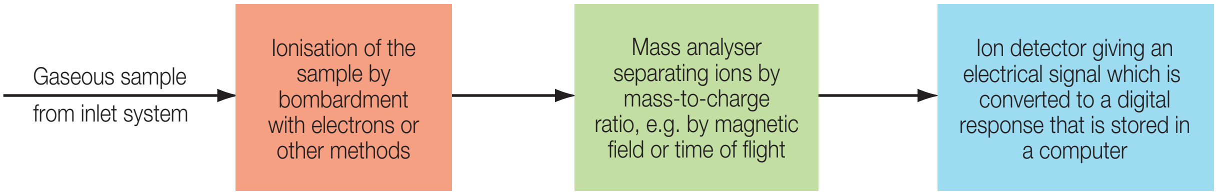

Gaseous sample
from inlet system
Ionisation of the sample by bombardment with electrons or other methods
Mass analyser separating ions by mass-to-charge ratio, e.g. by magnetic field or time of flight
Ion detector giving an electrical signal which is converted to a digital response that is stored in a computer

Figure 1.10 A schematic diagram to show the key features of a mass spectrometer.

Before atoms, or molecules, can be separated and detected in a mass spectrometer, they must be converted to positive ions in the gaseous or vapour state. This can be done in various ways. In some mass spectrometers, a beam of high-energy electrons bombards the atoms or molecules of the sample. This turns them into ions by knocking out one or more electrons.

$$\underset{\text{fast-moving electron}}{e^-} + \underset{\text{atom in sample vapour}}{X} \rightarrow \underset{\text{positive ion}}{X^+} + \underset{\text{electron knocked out of X}}{e^-} + \underset{\text{slower-moving electron}}{e^-}$$

Inside a mass spectrometer there is a high vacuum. This allows ionised atoms or molecules from the chemical being tested to be studied without interference from atoms and molecules in the air.

After ionisation, the charged species are separated to produce the mass spectrum, which distinguishes the positive ions on the basis of their **mass-to-charge** ratios.

Key term

The **mass-to-charge ratio** (*m*/*z*) is the ratio of the relative mass, *m*, of an ion to its charge, *z*, where *z* is the number of charges (1, 2 and so on). Spectrometers usually operate so that most ions produced have the value of $z = 1$.

There are various types of mass spectrometer. They differ in the method used to separate ions with different ratios of mass to charge. One type uses an electric field to accelerate ions into a magnetic field, which then deflects the ions onto the detector. A second type accelerates the ions and then separates them by their flight time through a field-free region. A third type, the so-called transmission quadrupole instrument, is now much the most common because it is very reliable, compact and easy to use. It varies the fields in the instrument in a subtle way to allow ions with a particular mass-to-charge ratio to pass through to the detector at any one time.

The output from the detector of a mass spectrometer is often presented as a 'stick diagram'. This shows the strength of the signal produced by ions of varying mass-to-charge ratio. The scale on the vertical axis shows the relative abundance of the ions. The horizontal axis shows the *m*/*z* values.

Each of the four peaks on the mass spectrum of lead in Figure 1.11 represents a lead ion of different mass, and the heights of the peaks give the proportions of the ions present.

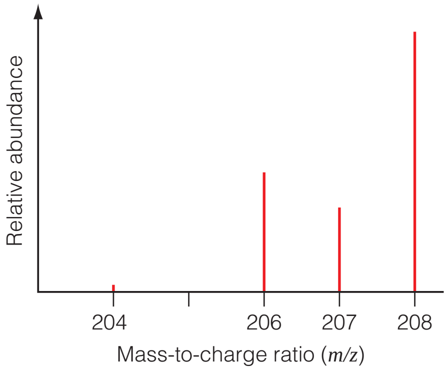


Figure 1.11 A mass spectrum of the element lead. The lead ions that produce the peaks in the mass spectrum are all 1+ ions formed by ionising atoms in a lead vapour at very low pressure. The lead ions that form under these conditions are not the same as the stable lead ions normally found in solid lead compounds or in solutions.

Test yourself

11 Look carefully at Figure 1.11.

- **a)** How many different ions are detected in the mass spectrum of lead?
- **b)** What are the relative masses of these different ions?
- **c)** Make a rough estimate of the relative proportions of these different ions in the sample of lead.

1.4 Isotopes and relative isotopic masses

Mass spectrometer traces, like that in Figure 1.11, show that lead and most other elements contain atoms that are not exactly alike. When atoms of these elements are ionised in a mass spectrometer, the ions separate and are detected as two or more peaks with different values of m/z. This shows that the atoms from which the ions formed must have different relative masses. These atoms of the same element with different masses are called **isotopes**.

Look closely at Figure 1.12. It shows a mass spectrometer print out (mass spectrum) for magnesium. The three peaks show that magnesium consists of three isotopes with relative masses of 24, 25 and 26. These relative masses are best described as **relative isotopic masses** because they give the relative mass of particular isotopes.

Chemists originally measured the relative masses of atoms relative to hydrogen. Then, because of the existence of isotopes, it became necessary to choose one particular isotope as the standard. Today, the isotope carbon-12 ($^{12}_{6}C$) is chosen as the standard and given a relative mass of exactly 12.

The heights of the peaks in Figure 1.12 show the relative proportions of the three isotopes. The isotope magnesium-24 has a mass number of 24 with 12 protons and 12 neutrons, whereas magnesium-25 has a mass number of 25 with 12 protons and 13 neutrons. Table 1.2 summarises the important similarities and differences in isotopes.

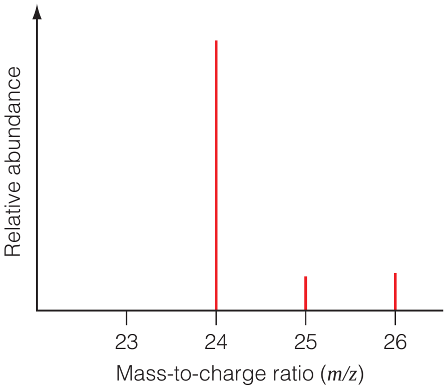


Figure 1.12 A mass spectrum for magnesium.

Key terms

Isotopes are atoms of the same element which have the same number of protons in the nucleus but a different number of neutrons. So isotopes have the same atomic number but different mass numbers.

Relative isotopic mass is the mass of one atom of an isotope relative to $\frac{1}{12}$th of the mass of an atom of the isotope carbon-12. The values are relative so they do not have units.

Relative atomic mass, A_r, is the average mass of an atom of an element relative to $\frac{1}{12}$th of the mass of an atom of the isotope carbon-12. The values are relative so they do not have units.

Table 1.2 Similarities and differences in isotopes.

Isotopes have the same	Isotopes have different
• number of protons • number of electrons • atomic number • chemical properties	• numbers of neutrons • mass numbers • physical properties

Relative atomic masses

The relative atomic mass of an element is the average mass of an atom of the element relative to one twelfth the mass of an atom of the isotope carbon-12. The symbol for **relative atomic mass** is A_r, where 'r' stands for relative.

$$\text{relative atomic mass} = \frac{\text{average mass of an atom of the element}}{\frac{1}{12} \times \text{the mass of one atom of carbon-12}}$$

Using this scale, the relative atomic mass of hydrogen is 1.0, that of helium is 4.0, and that of oxygen is 16.0. This can be written as: $A_r(H) = 1.0$, $A_r(He) = 4.0$ and $A_r(O) = 16.0$, or simply H = 1.0, He = 4.0 and Cl = 35.5 for short (Figure 1.13).

The values of relative atomic masses have no units because they are relative. The relative atomic masses of all elements are shown in the periodic table on page 314.

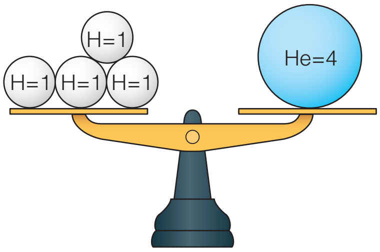


Figure 1.13 If atoms could be weighed, the scales would show that helium atoms are four times as heavy as hydrogen atoms.

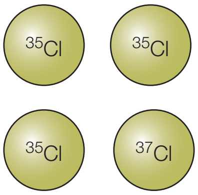


Figure 1.14 On average, for every four chlorine atoms, three are chlorine-35 and one is chlorine-37.

The accurate relative atomic masses of most elements in tables of data are not whole numbers. This is because these elements contain a mixture of isotopes. For example, chlorine contains two isotopes, chlorine-35 and chlorine-37, in the relative proportions of 3 : 1 (Figure 1.14). This is $\frac{3}{4}$, or 75%, chlorine-35 and $\frac{1}{4}$, or 25%, chlorine-37.

So, the average mass of a chlorine atom on the ^{12}C scale is given by:

$$\frac{(3 \times 35) + (1 \times 37)}{4} = 35.5$$

This is the relative atomic mass of chlorine.

Tip

The relative masses of individual isotopes are called **relative isotopic masses**, whereas the relative masses of the atoms in an element (often containing a mixture of isotopes) are called **relative atomic masses**.

Example

The mass spectrum of magnesium (Figure 1.12) shows that it consists of three isotopes with these percentage abundances:

magnesium-24: 78.6%

magnesium-25: 10.1%

magnesium-26: 11.3%

Calculate the relative atomic mass of magnesium.

Notes on the method

The relative atomic mass of magnesium is an average value that takes into account the relative masses of its isotopes and their relative abundance. It is a 'weighted' average (Section A1.4).

The percentages show you how many atoms of each isotope are present in a sample of 100 atoms.

Answer

The total relative mass of 100 atoms of magnesium

$$= (78.6 \times 24) + (10.1 \times 25) + (11.3 \times 26) = 2432.7$$

The average relative mass of a magnesium atom = 2432.7 ÷ 100 = 24.3 (to three significant figures)

Tip

The values for A_r are average values for the mixture of isotopes found naturally. This means that the values of relative atomic masses are often not whole numbers. In calculations you should use A_r values to one decimal place, as in the periodic table on page 314.

Test yourself

12 Look up the values of relative atomic masses in the periodic table on page 314. How many times heavier (to the nearest whole number) are:

- **a)** C atoms than H atoms
- **b)** Mg atoms than C atoms
- **c)** S atoms than He atoms
- **d)** C atoms than He atoms
- **e)** Fe atoms than N atoms?

13 Silicon consists of three naturally occurring isotopes, $^{28}_{14}Si$ (93.0%), $^{29}_{14}Si$ (5.0%) and $^{30}_{14}Si$ (2.0%).

- **a)** How many protons and neutrons are present in the nuclei of each of these isotopes?
- **b)** What is the relative atomic mass of silicon?

14 Neon has two isotopes with mass numbers of 20 and 22.

- **a)** How do you think the boiling temperature of neon-20 compares with that of neon-22? Explain your answer.
- **b)** Neon in the air contains 90% neon-20 and 10% neon-22. What is the relative atomic mass of neon in the air?

15 Why do isotopes have the same chemical properties, but different physical properties?

Relative molecular and formula masses

Relative atomic masses can also be used to compare the masses of different molecules. The relative masses of molecules are called relative molecular masses (symbol M_r).

The **relative molecular mass** of an element or compound is the sum of the relative atomic masses of all the atoms in its molecular formula.

For oxygen, O_2, $M_r(O_2) = 2 \times A_r(O) = 2 \times 16.0 = 32.0$

and for sulfuric acid, $M_r(H_2SO_4) = 2 \times A_r(H) + A_r(S) + 4 \times A_r(O)$

$= (2 \times 1.0) + 32.1 + (4 \times 16.0) = 98.1$

Metal compounds consist of giant structures of ions and not molecules. To avoid the suggestion that their formulae represent molecules, chemists use the term **relative formula mass** (symbol M_r), not relative molecular mass, for ionic compounds and for other compounds with giant structures such as silicon dioxide, SiO_2.

For magnesium nitrate,

$$M_r(Mg(NO_3)_2) = A_r(Mg) + 2 \times [A_r(N) + 3 \times A_r(O)]$$
$$= 24.3 + 2 \times (14.0 + 48.0) = 148.3$$

Key terms

The **relative molecular mass** of an element or compound is the sum of the relative atomic masses of all the atoms in its molecular formula.

The **relative formula mass** of a compound is the sum of the relative atomic masses of all the atoms in its formula.

Tip

Section A1.1 of Appendix A1 on page 286 gives advice on how to work out the value of maths equations with brackets and combinations of multiplication and addition.

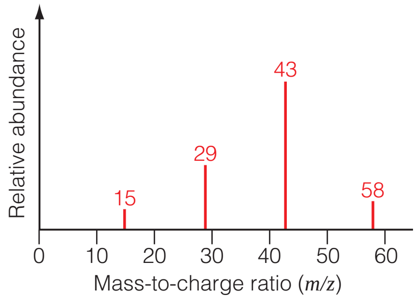


Figure 1.15 The mass spectrum of a hydrocarbon and its fragments.

Mass spectrometers can also be used to study molecules (Chapter 7). After injecting a sample into the instrument and vaporising it, bombarding electrons not only ionise the molecules but also break them into fragments. Because of the high vacuum inside the mass spectrometer, it is possible to study these molecular fragments and ions which do not normally exist. As a result the mass spectrum consists of a 'fragmentation pattern' (Figure 1.15). When analysing molecular compounds, the peak of the ion with the highest mass is usually the whole molecule ionised. So the mass of this 'parent ion' or 'molecular ion', M^+, is the relative molecular mass of the compound.

$$\underset{\text{high-energy electron}}{e^-} + \underset{\text{molecule in sample}}{M(g)} \longrightarrow \underset{\text{molecular ion}}{M^+} + \underbrace{e^- + e^-}_{\text{electrons}}$$

Test yourself

16 What is the relative molecular mass of:

- **a)** chlorine, Cl_2
- **b)** sulfur, S_8
- **c)** ethanol, C_2H_5OH
- **d)** tetrachloromethane, CCl_4?

17 What is the relative formula mass of:

- **a)** magnesium chloride, $MgCl_2$
- **b)** iron(III) oxide, Fe_2O_3
- **c)** hydrated copper(II) sulfate, $CuSO_4.5H_2O$?

18 Look carefully at Figure 1.15.

- **a)** What is the relative molecular mass of the hydrocarbon?
- **b)** The fragment of the hydrocarbon with relative mass 15 is a CH_3 group. What do you think the fragments are with relative masses of 29 and 43?
- **c)** Draw a possible structure for the hydrocarbon.

Notice that, by carefully interpreting the data from mass spectrometers, chemists can deduce:

- the isotopic composition of elements
- the relative atomic masses of elements
- the relative molecular masses of compounds.

Chemists who separate and synthesise new compounds can also identify the fragments in the mass spectra of these compounds. Then, by piecing the fragments together, they can identify possible structures for the new compounds.

The combination of gas chromatography and mass spectrometry is particularly important in modern chemical analysis. Chromatography is first used to separate the chemicals in an unknown mixture, such as polluted water or similar compounds synthesised for possible use as drugs. Then mass spectrometry is used to detect and identify the separated components.

Activity

Mass spectrometry in sport

Mass spectrometry provides an incredibly sensitive method of analysis in areas such as space research, medical research, monitoring pollutants in the environment and the detection of illegal drugs in sport.

Detecting the use of anabolic steroids in sport

Since the 1980s, unscrupulous sportsmen and sportswomen have tried to improve their performance by using anabolic steroids. These drugs increase muscle size and strength, which increases the chance of winning (Figure 1.16). But anabolic steroids also have serious harmful effects on the body. Women develop masculine features and anyone using them may suffer heart disease, liver cancer and depression leading to suicide.

Figure 1.16 Ben Johnson won the men's 100 m race at the Olympic Games in 1992. Unfortunately, urine tests showed that he had used anabolic steroids – Johnson was stripped of his title and the gold medal.

Sporting bodies, such as the International Olympic Committee, have banned the use of anabolic steroids in all sports and have introduced a rigorous testing regime. The testing procedures involve analysis of urine samples using mass spectrometry.

Great care is taken during sampling, transport, storage and analysis to ensure that the results of analysis will stand up in court.

Figure 1.17 shows the molecular ion and the largest fragments in the mass spectrum of a banned chemical that is thought to be dihydrocodeine ($C_{18}H_{23}O_3N$).

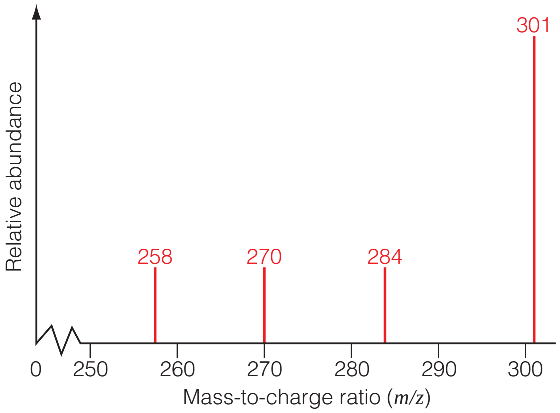


Figure 1.17 The molecular ion and the largest fragments in the mass spectrum of a banned chemical.

1. What is the probable relative molecular mass of the banned chemical on the mass spectrum?
2. Is the probable relative molecular mass consistent with that of dihydrocodeine, ($C_{18}H_{23}O_3N$)? Explain your answer.
3. What is the relative mass of the fragment *lost* from one molecule of the banned substance, leaving the fragment of relative mass 284?
4. Dihydrocodeine contains a CH_3O– group and an –OH group. What evidence does the mass spectrum provide for these two groups?

1.5 Evidence for the electronic structure of atoms

In a mass spectrometer, a beam of electrons can be used to bombard the sample, turning atoms (or molecules) into positive ions. The electrons in the beam must have enough energy to knock electrons off atoms in the sample. By varying the intensity of the beam, it is possible to measure the minimum amount of energy needed to remove electrons from the atoms of an element. From these measurements, scientists can predict the electron structures of atoms.

Key terms

An **ionisation energy** is the energy needed to remove one mole of electrons from one mole of gaseous atoms, or ions, of an element.

Atomic **energy levels** are the energies of electrons in atoms. According to quantum theory, each electron in an atom has a definite energy. When atoms gain or lose energy, the electrons jump from one energy level to another.

Tip

The shells of electrons at fixed or specific levels are sometimes called **quantum shells**. The word ‘quantum’ is used to describe something related to a fixed amount or a fixed level.

The energy needed to remove one electron from each atom in one mole of gaseous atoms is known as the first **ionisation energy**. The product is one mole of gaseous ions with one positive charge.

So, the first ionisation energy of sodium is the energy required for the process

$$Na(g) \rightarrow Na^+(g) + e^- \qquad \text{first ionisation energy} = +496\,kJ\,mol^{-1}$$

Ionisation energies like this are always endothermic. Energy is taken in by the reaction so the energy change is given a positive sign.

Scientists can also determine ionisation energies by using a spectroscope to study the light given out by atoms when heated in a flame (as in a flame test). The spectroscope shows up a series of bright lines (Figure 1.18). Heating the atoms gives them energy which makes some of the electrons jump to higher **energy levels**. Each line in the spectrum arises from the energy given out as the electrons drop back from a higher energy level to a lower level.

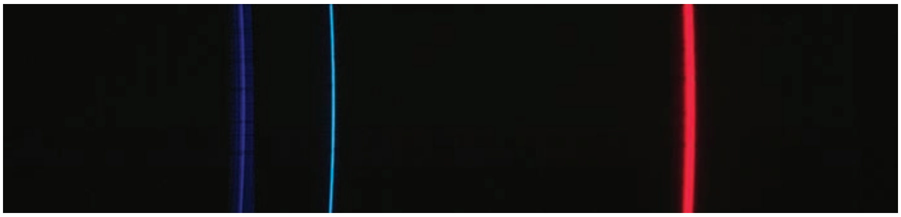


Figure 1.18 The line spectrum of hydrogen in the visible region of the electromagnetic spectrum.

Using data from spectra, it is possible to measure the energy required to remove electrons from ions with increasing charges. A succession of ionisation energies is obtained. For example:

$$Na(g) \rightarrow Na^+(g) + e^- \qquad \text{first ionisation energy} = +496\,kJ\,mol^{-1}$$

$$Na^+(g) \rightarrow Na^{2+}(g) + e^- \qquad \text{second ionisation energy} = +4563\,kJ\,mol^{-1}$$

$$Na^{2+}(g) \rightarrow Na^{3+}(g) + e^- \qquad \text{third ionisation energy} = +\ 6913\,kJ\,mol^{-1}$$

There are 11 electrons in a sodium atom so there are 11 successive ionisation energies for this element.

The successive ionisation energies for an element get bigger and bigger. This is not surprising because, having removed one electron, it is more difficult to remove a second electron from the positive ion formed.

The graph in Figure 1.19 provides evidence to support the theory that the electrons in an atom are arranged in a series of levels or shells around the nucleus.

Tip

Logarithms reduce the range of numbers that vary over several orders of magnitude. Figure 1.19 uses logarithms which work like this: log 10 = 1, log 100 = 2, log 1000 = 3 and so on. A calculator can be used to find the values of the logarithms (log) of other numbers.

Notice the big jumps in value between the first and second ionisation energies, and between the ninth and tenth ionisation energies in Figure 1.19. This suggests that sodium atoms have one electron in an outer shell or energy level furthest from the nucleus. This outer electron is relatively easily removed because it is **shielded** from the full attraction of the positive nucleus by 10 inner electrons.

Below this outer single electron, sodium atoms appear to have eight electrons in a second shell, all at roughly the same energy level. These eight electrons are closer to the nucleus than the single outer electron.

Finally, sodium atoms have two inner electrons in a shell closest to the nucleus. These two electrons feel the full attraction of the positive nucleus and are hardest to remove with the most endothermic ionisation energies.

This electronic structure for a sodium atom can be represented in an energy level diagram as in Figure 1.20. The electron arrangement in sodium can sometimes be written simply as 2, 8, 1 (but see Section 1.6).

In energy level diagrams such as that in Figure 1.20, the electrons are represented by arrows. When an energy level is filled, the electrons are paired up and in each of these pairs the electrons are spinning in opposite directions. Chemists have found that paired electrons can only be stable when they spin in opposite directions so that the magnetic attraction resulting from their opposite spins can counteract the electrical repulsion from their negative charges.

In energy level diagrams such as Figure 1.20, the opposite spins of the paired electrons are shown by drawing the arrows in opposite directions.

The quantum shells of electrons correspond to the periods of elements in the periodic table. By noting where the first big jump comes in the successive ionisation energies of an element, it is possible to predict the group to which the element belongs. For example, the first big jump in the successive ionisation energies for sodium comes after the first electron is removed. This suggests that sodium has just one electron in its outermost shell and, therefore, it must be in Group 1.

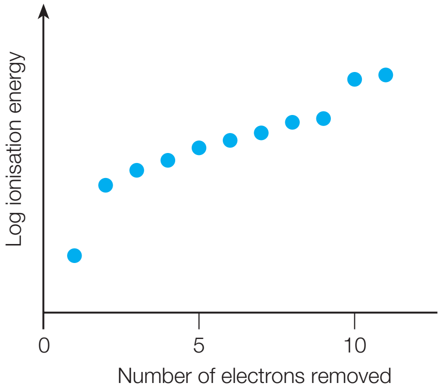


Figure 1.19 Log ionisation energy against the number of electrons removed for sodium. The values for the ionisation energies range from 496 kJ mol^{-1} to 159 079 kJ mol^{-1}. Plotting the logarithms of these values makes it possible to fit them on to the vertical axis, while still showing where there are big jumps in the values.

Key term

Shielding is an effect of inner electrons which reduces the pull of the nucleus on the electrons in the outer shell of an atom. Thanks to shielding, the electrons in the outer shell are attracted by an ‘effective nuclear charge’ which is less than the full charge on the nucleus.

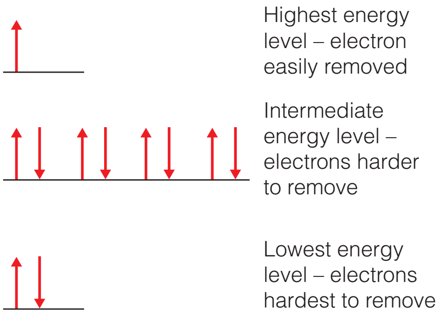

Highest energy level – electron easily removed
Intermediate energy level – electrons harder to remove
Lowest energy level – electrons hardest to remove

Figure 1.20 The energy levels of electrons in a sodium atom.

Test yourself

19 Write equations to represent:

- **a)** the second ionisation energy of calcium
- **b)** the third ionisation energy of aluminium.

20 The successive ionisation energies of beryllium are 900, 1757, 14 849 and 21 007 kJ mol^{-1}.

- **a)** What is the atomic number of beryllium?
- **b)** Why do successive ionisation energies always get more endothermic?
- **c)** Draw an energy level diagram for the electrons in beryllium, and predict its electron structure.
- **d)** To which group in the periodic table does beryllium belong?

Activity

Evidence for sub-shells of electrons

By studying the first ionisation energies of successive elements in the periodic table, it is possible to compare how easy it is to remove an electron from the highest energy level in the atoms of these elements. This provides us with evidence for the arrangement of electrons in sub-shells.

1 Refer to the data sheet for Chapter 1, 'The first ionisation energies of successive elements in the periodic table', which you can access via the QR code for this chapter on page 312. Using this data, plot a graph of the first ionisation energy for the first 20 elements in the periodic table. Put first ionisation energy on the vertical axis and atomic number on the horizontal axis.

2 When you have plotted the points, draw lines from one point to the next to show a pattern of peaks and troughs. Label each point with the symbol of its corresponding element.

3 **a)** Where do the alkali metals in Group 1 appear in the pattern?

  b) Where do the noble gases in Group 0 appear in the pattern?

4 What similarities do you notice in the pattern for elements in Period 2 (lithium to neon) with that for elements in Period 3 (sodium to argon)?

5 Identify three sub-groups of points in both Period 2 and Period 3. How many elements are there in each sub-group?

1.6 Electrons in energy levels

From the study of ionisation energies and spectra, scientists have found that the electrons in atoms are grouped together in energy levels or quantum shells. The numbers 1, 2, 3, etc. are used to label these main shells, starting nearest to the nucleus.

Each quantum shell can hold only a limited number of electrons:

- the $n = 1$ shell can hold 2 electrons
- the $n = 2$ shell can hold 8 electrons
- the $n = 3$ shell can hold 18 electrons
- the $n = 4$ shell can hold 32 electrons.

These main shells divide into sub-shells labelled s, p, d and f. The labels s, p, d and f are left over from the early studies of the spectra of different elements. These studies used the words 'sharp', 'principal', 'diffuse' and 'fundamental' to describe different lines in the spectra. The terms have no special significance now.

The sub-shells are further divided into **atomic orbitals** (Figure 1.21). Each orbital is defined by its:

- energy level
- shape
- direction in space.

The shapes and directions in space of the atomic orbitals are found by calculating the *probability* of finding an electron at any point in an atom. These calculations are based on a theoretical model described by the Schrödinger wave equation. The one orbital in the first shell is spherical. It is an example of an s orbital (1s). The four orbitals in the second shell are made up of one s orbital (2s) and three dumbbell-shaped p orbitals. The three p orbitals ($2p_x$, $2p_y$, $2p_z$) are arranged at right angles to each other along the x-, y- and z-axes (Figure 1.22).

Key term

Atomic orbitals are the sub-divisions of the electron shells in atoms. The main shells divide into sub-shells labelled s, p, d and f. The sub-shells are further divided into atomic orbitals. An orbital is a region in space around the nucleus of an atom in which there is a 95% chance of finding an electron, or a pair of electrons with opposite spins.

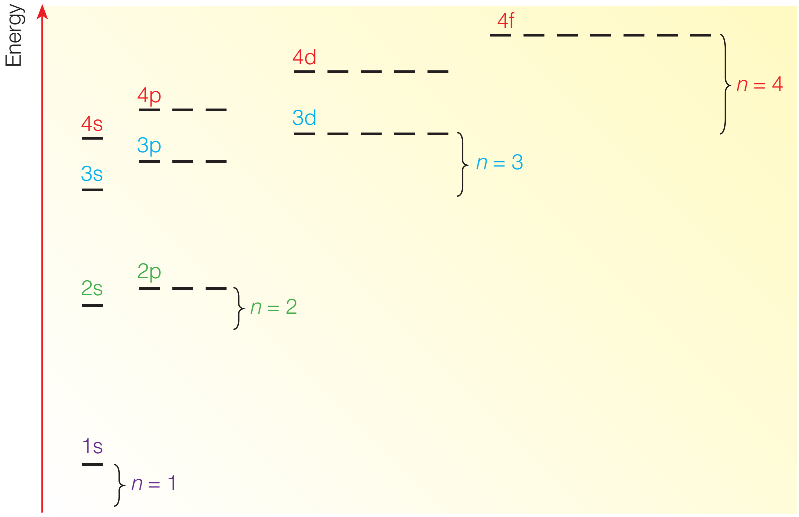


Figure 1.21 The energies of atomic orbitals in atoms. The terms 'energy level' and 'orbital' are often used interchangeably. In a free atom the orbitals in a sub-shell have the same energy.

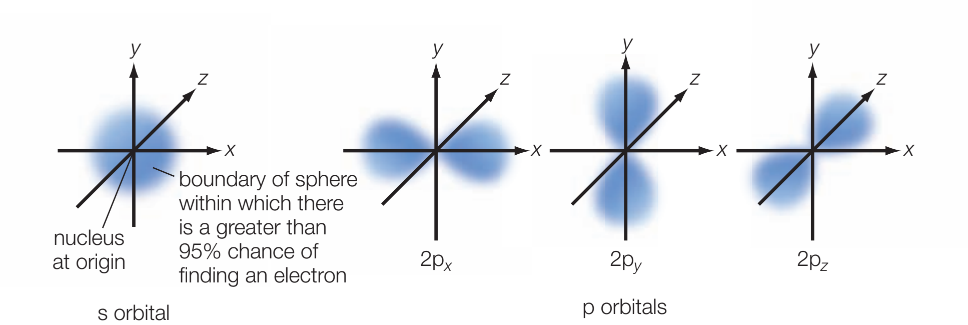

y
z
x
nucleus at origin
boundary of sphere within which there is a greater than 95% chance of finding an electron
s orbital
2p$_x$
2p$_y$
2p$_z$
p orbitals

Figure 1.22 The shapes of s and p atomic orbitals. The density of shading indicates the probability of finding an electron at any point.

The electrons in an atom fill the energy levels according to a set of rules which determine electron arrangements in atoms.

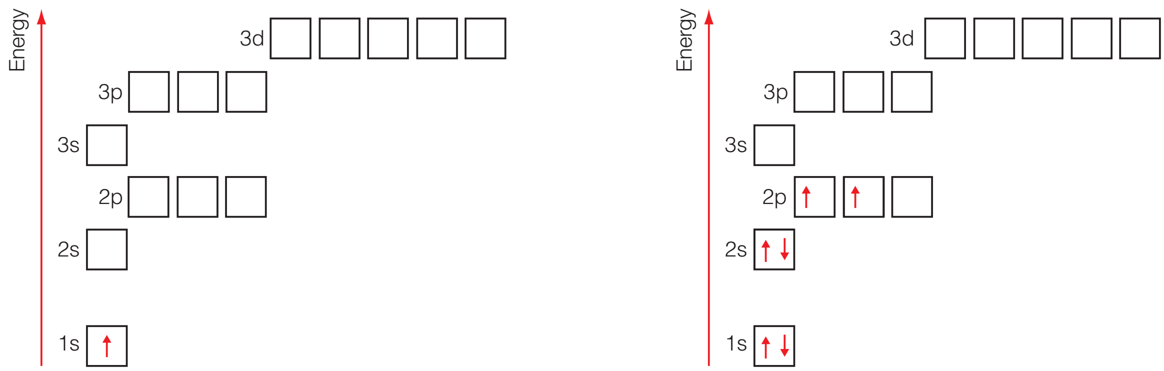
The three rules are:

- electrons go into the orbital with the lowest available energy level first
- each orbital can only contain at most two electrons (with opposite spins)
- where there are two or more orbitals at the same energy, they fill singly before the electrons pair up.

The application of these rules is illustrated for the atoms of four elements in Figure 1.23. These descriptions of the arrangement of electrons in the atoms of elements are called **electron configurations**. Chemists sometimes use the term 'aufbau principle' for these rules from the German word meaning 'build up'. This is a reminder that electron configurations build up from the bottom. There are several common conventions for representing electron configurations in a shorthand way. Figure 1.24, for example, shows the electrons-in-boxes representations and the s, p, d, f notations for the electronic structures of beryllium, nitrogen and sodium.

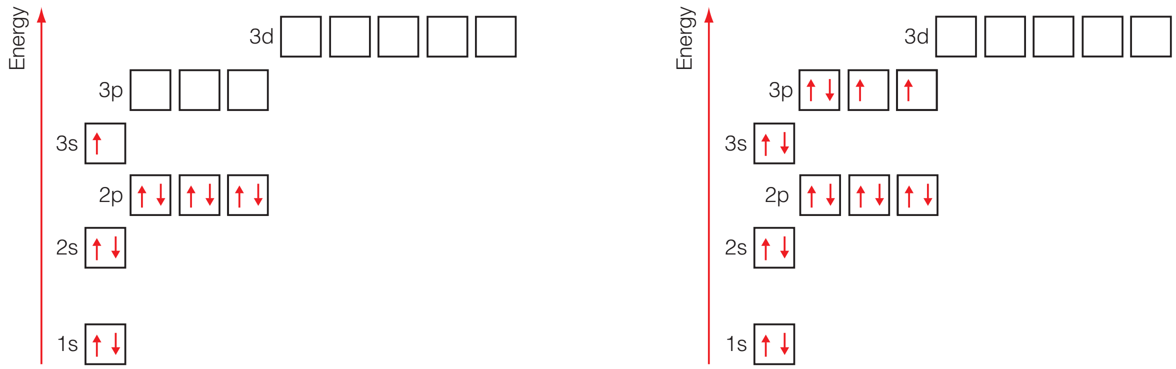
Key term

The **electron configuration** of an element describes the number and arrangement of electrons in an atom of the element. A shortened form of electron configuration uses the symbol of the previous noble gas, in square brackets, to stand for the inner shells. So, using this convention, the electron configuration of sodium is [Ne]3s^1.


Energy
3d
3p
3s
2p
2s
1s
Energy
3d
3p
3s
2p
2s
1s

hydrogen, $1s^1$

carbon, $1s^2 2s^2 2p^2$


Energy
3d
3p
3s
2p
2s
1s
Energy
3d
3p
3s
2p
2s
1s

sodium, $1s^2 2s^2 2p^6 3s^1$

sulfur, $1s^2 2s^2 2p^6 3s^2 3p^4$

Figure 1.23 Electrons in energy levels for four atoms to show the application of the building-up principle.

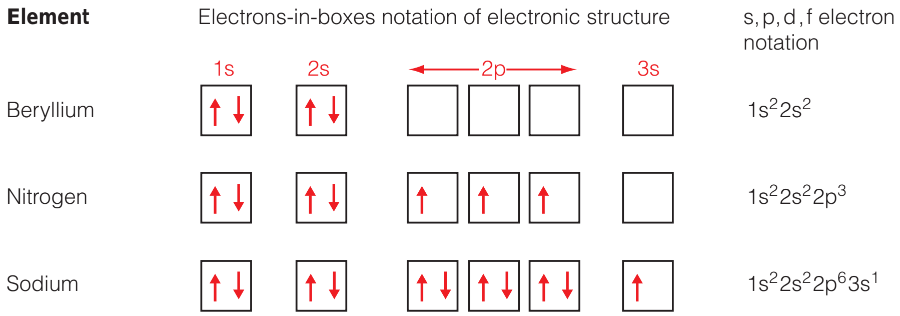

Element
Electrons-in-boxes notation of electronic structure
s, p, d, f electron notation
1s
2s
2p
3s
Beryllium
$1s^2 2s^2$
Nitrogen
$1s^2 2s^2 2p^3$
Sodium
$1s^2 2s^2 2p^6 3s^1$

Figure 1.24 Electrons-in-boxes representations and s, p, d, f notations for the electronic structure of beryllium, nitrogen and sodium.

Test yourself

21 Sketch a graph of log ionisation energy against number of electrons removed when all the electrons are successively removed from a phosphorus atom. (Sketch the graph in the style of Figure 1.19. There is no need to look up logarithms.)

22 Write out the electron structure in terms of shells (for sodium this would be 2, 8, 1) for the atoms of following elements:

a) lithium

b) oxygen

c) neon

d) silicon.

23 Write the electronic sub-shell structure for the elements in Question 22 – for sodium this would be $1s^22s^22p^63s^1$.

24 Draw the electrons-in-boxes representations for the following elements:

a) boron **b)** fluorine

c) phosphorus **d)** potassium.

25 Identify the elements with the following electron structures in their outermost shells:

a) $1s^2$ **b)** $2s^22p^2$

c) $3s^2$ **d)** $3s^23p^4$.

The development of knowledge and understanding about electronic structures illustrates how chemists use the results of their experiments, such as the measurements of ionisation energies, to devise atomic models that they can use to explain the properties of elements. It also illustrates the important distinction between evidence and experimental data on the one hand, and ideas, theories and explanations on the other.

In particular, ionisation energies and spectra have provided chemists with evidence and information that has caused them to develop and modify their models and theories about electron structure. Early ideas about electrons arranged in shells have been developed to take in the evidence for sub-shells, and then modified to include ideas about orbitals.

1.7 Electron structures and the periodic table

The periodic table helps chemists to bring order and patterns to the vast amount of information they have discovered about all the elements and their compounds.

In the modern periodic table, elements are arranged in order of atomic number. The horizontal rows in the table are called **periods** – each period ends with a noble gas. The vertical columns in the table are called **groups** which can be divided into four blocks – the s block, p block, d block and f block – based on the electron structures of the elements (Figure 1.25).

So, the modern arrangement of elements in the periodic table reflects the underlying electronic structures of the atoms, while the more sophisticated model of electron structure in terms of orbitals allows chemists to explain the properties of elements more effectively. The four blocks in the periodic table are shown in different colours in Figure 1.25.

- The *s block* comprises the reactive metals in Group 1 and Group 2 – such as potassium, sodium, calcium and magnesium. In these metals, the outermost electron is in an s orbital in the outer shell.
- The *p block* comprises the elements in Groups 3, 4, 5, 6, 7 and 0 on the right of the periodic table. These elements include relatively unreactive metals such as tin and lead, plus all the non-metals. In these elements, the last electron added goes into a p orbital in the outer shell.

Key terms

A **period** is a horizontal row of elements in the periodic table.

A **group** is a vertical column of elements in the periodic table. Elements in the same group have similar properties because they have the same outer electron configuration.

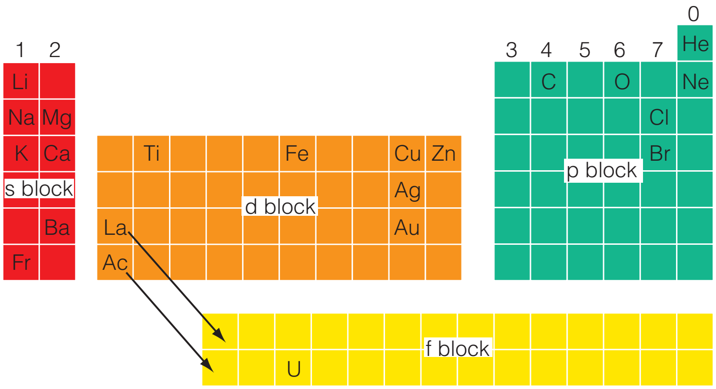


Figure 1.25 The s, p, d and f blocks in the periodic table.

- The *d-block* elements occupy a rectangle across Periods 4, 5, 6 and 7 between Group 2 and Group 3. The d-block elements are all metals – including titanium, iron, copper and silver – in which the last electron added goes into a d orbital. These metals are much less reactive than the s-block metals in Groups 1 and 2. Within the d block there are marked similarities across the periods, as well as the usual vertical similarities. The d-block elements are sometimes loosely called 'transition metals'.
- The *f-block* elements occupy a low rectangle across Periods 6 and 7 within the d block, but they are usually placed below the main table to prevent it becoming too wide to fit the page. Like the d-block elements, those in the f block are all metals. Here, the last added electron is in an f orbital. The f-block elements are often called the lanthanoids and actinoids because they are the 14 elements immediately following lanthanum, La, and actinium, Ac, in the periodic table. Another name used for the f-block elements is the 'inner transition elements'.

Tip

The International Union of Pure and Applied Chemistry (IUPAC) now recommends that the groups in the periodic table should be numbered from 1 to 18. Groups 1 and 2 are the same as before. Groups 3 to 12 are the vertical families of d-block elements. The groups traditionally numbered 3 to 7 and 0 then become Groups 13 to 18.

As the shells of electrons around the nuclei of atoms get further from the nucleus, they become closer in energy (see Figure 1.21). Therefore, the difference in energy between the second and third shells is less than that between the first and second. When the fourth shell is reached there is, in fact, an overlap between the orbitals of highest energy in the third shell (the 3d orbital) and that of lowest energy in the fourth shell (the 4s orbital) (Figure 1.26). As a result the orbitals that fill in the fourth period are the 4s, 3d and 4p orbitals in that order. This accounts for the position of the d-block elements in the periodic table.

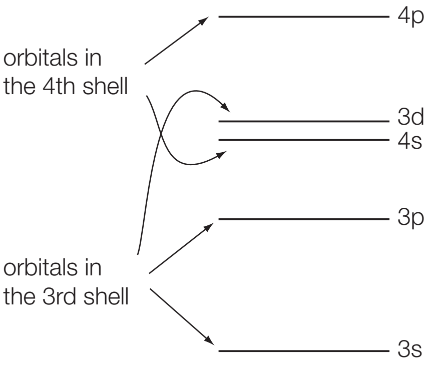


Figure 1.26 The relative energy levels of orbitals in the third and fourth shells.

Tip

The 4s orbital fills before the 3d orbital because it has a lower energy. However, the 4s orbital is the outer orbital and it is the electrons in the 4s orbital that are lost first when a d-block element ionises. Chromium and copper each only have one 4s electron in their atoms. The explanation for the irregularities lies in the stability of half-filled and filled sub-shells. So the electronic structure of chromium is [Ar]$3d^5 4s^1$ and that of copper is [Ar]$3d^{10} 4s^1$.

Table 1.3 shows the electron configurations of four elements in the fourth period. The rules for the order in which electrons fill orbitals still apply.

Element and symbol	Electronic structure				
	spdf notation	Electrons-in-boxes notation			
			3d	4s	←4p→
Potassium K	[Ar]$4s^1$	[Ar]	☐ ☐ ☐ ☐ ☐	↑	☐ ☐ ☐
Vanadium V	[Ar]$3d^3 4s^2$	[Ar]	↑ ↑ ↑ ☐ ☐	↑↓	☐ ☐ ☐
Iron Fe	[Ar]$3d^6 4s^2$	[Ar]	↑↓ ↑ ↑ ↑ ↑	↑↓	☐ ☐ ☐
Bromine Br	[Ar]$3d^{10} 4s^2 4p^5$	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑

Table 1.3 Electron configurations of four elements in the fourth period. [Ar] represents the electron configuration of argon: $1s^2 2s^2 2p^6 3s^2 3p^6$.

Test yourself

26 Write the electronic sub-shell structure for the atoms of these elements using spdf notation:

a) scandium **b)** manganese

c) zinc **d)** germanium.

27 Identify the elements with the following electron structures:

a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$

28 Write the electronic sub-shell structure for these ions using spdf notation:

a) Al^{3+} **b)** S^{2-}

c) Zn^{2+} **d)** Br^-

Groups

The elements in each group have similar properties because they have similar electron structures. This important point is well illustrated by the alkali metals in Group 1. Look at Figure 1.27 – notice that each alkali metal has one s electron in its outer shell. This similarity in their electron structures explains why they have similar properties.

Alkali metals:

- are very reactive because they lose their single outer electron so easily
- form ions with a charge of 1+ (Li^+, Na^+, K^+, etc.) so the formulae of their compounds are similar
- form very stable ions with an electron structure like that of a noble gas.

The chemical properties of all other elements are also determined by their electronic structures. Chemistry is largely about the electrons in the outer shells of atoms. The reactivity of an element depends on the number of electrons in the outer shell and how strongly they are held by the nuclear charge. This is a fundamental feature of chemistry and an essential principle which governs the way in which chemists think and work.

Group 1
The alkali metals
Lithium Li 2, 1 ($1s^2 2s^1$)
Sodium Na 2, 8, 1 ($1s^2 2s^2 2p^6 3s^1$)
Potassium K 2, 8, 8, 1 ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$)

Figure 1.27 Electron structures of the first three alkali metals.

Test yourself

29 Why are sodium and potassium so alike?

30 Why are the noble gases so unreactive?

31 **a)** Write down the electron shell structures and sub-shell structures of fluorine and chlorine in Group 7.

b) Why do you think fluorine and chlorine are so reactive with metals?

c) Why do the compounds of fluorine and chlorine with metals have similar formulae?

1.8 Periodic properties

Modern versions of the periodic table are all based on the one suggested by the Russian chemist Dmitri Mendeléev in 1869. When Mendeléev arranged the elements in order of atomic mass, he saw repeating patterns in their properties. A repeating pattern is a periodic pattern – hence the terms ‘periodic properties’ and ‘periodicity’.

Perhaps the most obvious repeating pattern in the periodic table is from metals on the left, through elements with intermediate properties (called metalloids), to non-metals on the right. Graphs of the physical properties of the elements – such as melting temperatures, electrical conductivities and first ionisation energies – against atomic number, also show repeating patterns. Using the models of bonding between atoms and molecules, chemists can explain the properties of elements and the repeating patterns in the periodic table.

Melting temperatures of the elements

Figure 1.28 shows the periodic pattern revealed by plotting the melting temperatures of elements against atomic number.

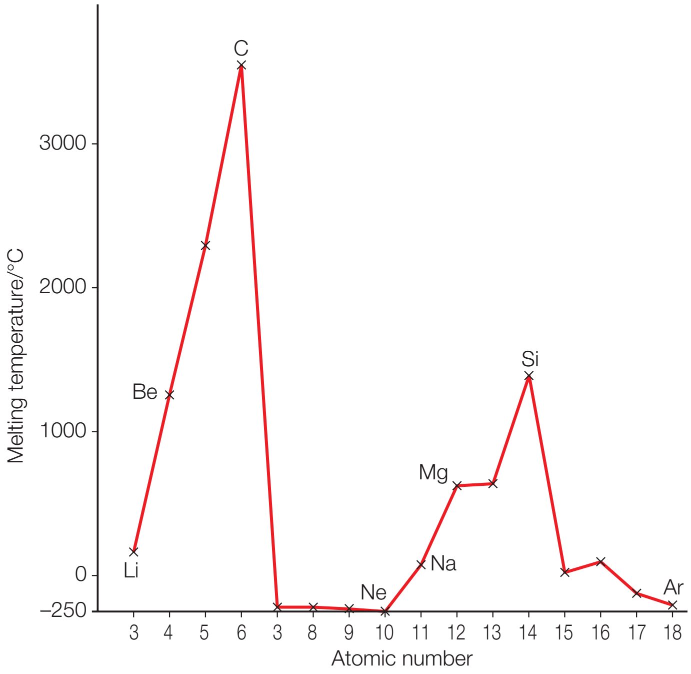


Figure 1.28 Periodicity in the melting temperatures of the elements.

The melting temperature of an element depends on both its structure and the type of bonding between its atoms. In metals, the bonding between atoms is strong (Section 2.9), so their melting temperatures are usually high. The more electrons each atom contributes from its outermost shell to the shared delocalised electrons, the stronger the bonding and the higher the melting temperature.

Therefore, melting temperatures rise from Group 1 to Group 2 to Group 3. In Group 4, the elements carbon and silicon have giant covalent structures. The bonds in these structures are strong and highly directional, so most of the bonds must break before the solid melts. This means that the melting temperatures of Group 4 elements are very high and at the peaks of the graph in Figure 1.28.

The non-metal elements in Groups 5, 6, 7 and 0 form simple molecules. The intermolecular forces between these simple molecules are weak, so these elements have low melting temperatures (Section 2.3).

First ionisation energies of the elements

Figure 1.29 shows the clear periodic trend in the first ionisation energies of the elements. The general trend is that first ionisation energies increase from left to right across a period.

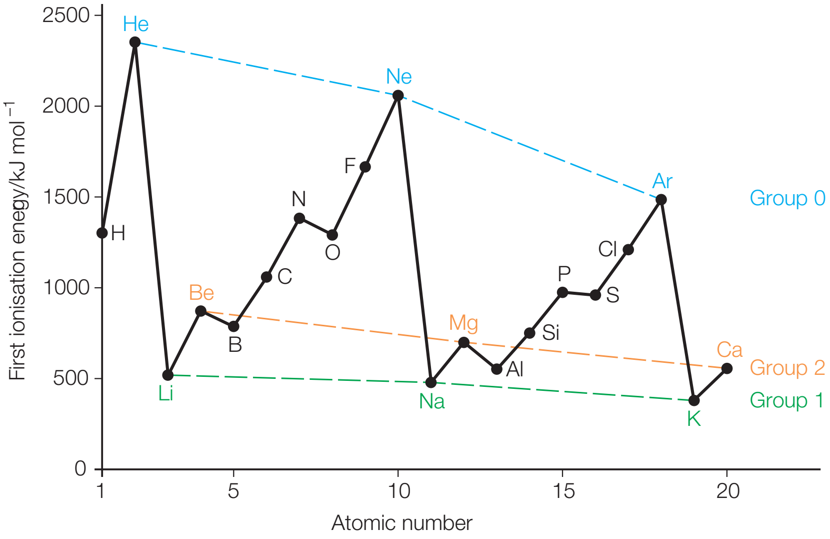


Figure 1.29 Periodicity in the first ionisation energies of the elements.

The ionisation energy of an atom is determined by three atomic properties.

- *The size of the positive nuclear charge*. As the positive nuclear charge increases, its attraction for outermost electrons increases and this tends to increase the ionisation energy.
- *The distance of the outermost electron from the nucleus*. As this distance increases, the attraction of the positive nucleus for the negative electron decreases and this tends to reduce the ionisation energy.

- *The shielding effect of electrons.* Electrons in inner shells exert a repelling effect on electrons in the outer shells of an atom. This reduces the pull of the nucleus on the electrons in the outer shell. Thanks to shielding, the 'effective nuclear charge' attracting electrons in the outer shell is much less than the full positive charge of the nucleus. As expected, the shielding effect increases as the number of inner shells increases.

Moving from left to right across any period, the nuclear charge increases as electrons are added to the same outer shell. The increasing nuclear charge tends to pull the outer electrons closer to the nucleus. The shielding effect of full inner shells is constant, the extra electrons in the same outer shell do not shield each other well so shielding hardly changes across the period. The increased nuclear charge and the reduced distance of the outer electrons from the nucleus makes the outer electrons more difficult to remove and, in general, the first ionisation energy increases.

But notice in Figure 1.29 that the rising trend in ionisation energies across a period is not smooth. There is a 2-3-3 pattern, which reflects the way in which electrons feed into s and p orbitals. The first ionisation energy decreases from beryllium to boron and again from nitrogen to oxygen.

A beryllium atom loses one of the $2s^2$ electrons from its outer shell when it ionises. The electron configuration of boron is $2s^22p^1$, so the electron lost when a boron atom ionises is a 2p electron. The 2p electron is in a higher energy sub-shell than a 2s electron, so it takes less energy to remove the boron 2p electron, despite the increase in nuclear charge.

The electron configuration of oxygen is $1s^22s^22p^4$. This means that one of the paired 2p electrons is removed on ionisation. In a nitrogen atom the electron configuration is $1s^22s^22p^3$ and all three p electrons are unpaired. Ionisation of nitrogen involves losing an unpaired electron. The repulsion between the negative electrons is greater for the paired electrons in the same sub-shell of an oxygen atom than between the unpaired electrons in a nitrogen atom. As a result it is easier to ionise an oxygen atom despite the increase in nuclear charge.

Test yourself

32 Why do the first ionisation energies of elements decrease with increasing atomic number in every group of the periodic table?

Exam practice questions

1 Antimony has two main isotopes – antimony-121 and antimony-123. A forensic scientist was asked to help a crime investigation by analysing the antimony in a bullet. This was found to contain 57.3% of ^{121}Sb and 42.7% of ^{123}Sb.

a) Define the term 'relative atomic mass'. *(3)*

b) Calculate the relative atomic mass of the sample of antimony from the bullet. Write your answer to an appropriate number of significant figures. *(3)*

c) State one similarity and one difference, in terms of sub-atomic particles, between the isotopes. *(2)*

2 This question concerns the following five species:

$^{16}_{8}O^{2-}$ $^{19}_{9}F^{-}$ $^{20}_{10}Ne$ $^{23}_{11}Na$ $^{25}_{12}Mg^{2+}$

a) Which two species have the same number of neutrons? *(2)*

b) Which two species have the same ratio of neutrons to protons? *(2)*

c) Which species does not have 10 electrons? *(1)*

3 a) Classify the elements with these electron configurations as s-, p- or d-block elements.

i) $1s^22s^22p^63s^2$

ii) $1s^22s^22p^63s^23p^4$

iii) $1s^22s^22p^63s^23p^63d^64s^2$ *(3)*

b) Use the electrons-in-boxes notation to give the electron configurations of:

i) a nitrogen atom

ii) a sodium ion

iii) a sulfide ion. *(3)*

4 The isotopes of magnesium, ^{24}Mg, ^{25}Mg and ^{26}Mg, can be separated by mass spectrometry.

a) Explain what you understand by the term 'isotope'. *(2)*

b) Copy and complete the table below to show the composition of the ^{24}Mg and ^{26}Mg isotopes. *(2)*

	Protons	Neutrons	Electrons
^{24}Mg			
^{26}Mg			

c) Copy and complete the electronic configuration of an atom of ^{24}Mg.

$1s^2$ __________ *(1)*

5 The table shows the melting temperatures of the elements in Period 3 of the periodic table.

Element	Melting temperature/°C
Na	98
Mg	649
Al	660
Si	1410
P	44
S	119
Cl	−101
Ar	−189

The trend in the melting temperatures across Period 3 and other periods is described as a periodic property.

a) What is the general pattern in melting temperatures across periods in the periodic table? *(2)*

b) How is this general trend related to the different types of elements? *(1)*

c) What do you understand by the term 'periodic property'? *(2)*

d) State two other properties which can be described as periodic in relation to the periodic table. *(2)*

6 The table shows the first and second ionisation energies of lithium and sodium in Group 1 of the periodic table.

Element	First ionisation energy/kJ mol^{-1}	Second ionisation energy/kJ mol^{-1}
Lithium	520	7298
Sodium	496	4563

a) Write an equation, with state symbols, for the second ionisation energy of sodium. *(2)*

b) Why are the second ionisation energies of lithium and sodium larger than their first ionisation energies? *(3)*

c) Why are the first and second ionisation energies of sodium smaller than those of lithium? *(4)*

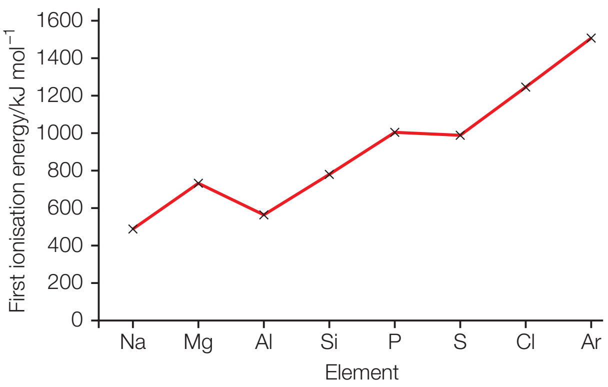
d) The first five successive ionisation energies, in kJ mol^{-1}, of an element, X, in Period 3 of the periodic table are 578, 1817, 2745, 11 578, 14 831.

  i) Identify element X. *(1)*

  ii) Explain how you obtained your answer. *(2)*

e) Predict which element in the periodic table has the highest first ionisation energy and explain your answer. *(3)*

7 The graph shows the first ionisation energies of the elements in Period 2 of the periodic table.



a) Describe and explain the *general* trend in first ionisation energies from Na to Ar. *(3)*

b) Explain why aluminium, Al, has a lower first ionisation energy than magnesium, Mg. *(2)*

c) Explain why the ionisation energy decreases from phosphorus, P, to sulfur, S. *(2)*

d) Predict the value for the first ionisation energy of potassium and explain your answer. *(2)*

e) The first five ionisation energies of an element are 738, 1451, 7733, 10 541, 13 629 kJ mol^{-1}. Explain why the element cannot have an atomic number less than 12. *(3)*

8 a) Bromine consists of two isotopes bromine-79 and bromine-81 which are equally abundant. Explain why the mass spectrum of bromine includes:

  i) two lines with *m/z* values of 79 and 81 with heights in the ratio 1 : 1 *(3)*

  ii) three lines with *m/z* values of 158, 160 and 162 with heights in the ratio 1 : 2 : 1. *(3)*

b) Chlorine consists of two isotopes chlorine-35 and chlorine-37. Explain why the mass spectrum of chlorine includes:

  i) two lines with *m/z* values of 35 and 37 with heights in the ratio 3 : 1 *(2)*

  ii) three lines with *m/z* values of 70, 72 and 74 with heights in the ratio 9 : 6 : 1. *(3)*

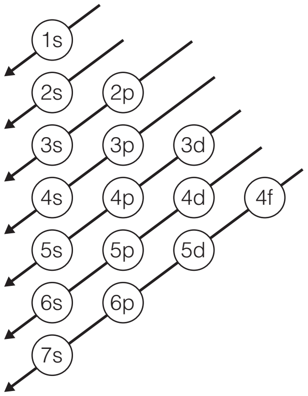
c) Account for these features of the mass spectrum of dichloroethene, $C_2H_2Cl_2$ ($M_r = 97$):

  i) the absence of a peak at $m/z = 97$ (2)

  ii) the presence of three peaks at *m/z* values of 96, 98 and 100 with intensities in the ratio 9 : 6 : 1 *(3)*

  iii) the presence of two peaks at *m/z* values of 61 and 63 with intensities in the ratio 3 : 1. *(3)*

9 This diagram shows the order in which sub-shells are filled by electrons according to the Aufbau principle which accounts for the arrangement of elements in the modern form of the periodic table.



a) How does this diagram account for the position of the d-block elements in the periodic table? *(2)*

b) What is the electron configuration of tin (atomic number 50)? *(1)*

c) Explain why this diagram cannot account for elements with atomic numbers greater than 88. *(2)*

d) How many orbitals are there in the 4f sub-shell? Show how you decide on your answer. *(2)*

e) What can you deduce about the relative energies of the 4f and 5d orbitals given the electron configurations of the four elements with atomic numbers from 57 to 60?

Lanthanum: $[Xe]4f^0 5d^1 6s^2$
Cerium: $[Xe]4f^2 5d^0 6s^2$
Praseodymium: $[Xe]4f^3 5d^0 6s^2$
Neodymium: $[Xe]4f^4 5d^0 6s^2$

How does this information, and the diagram above, account for the position of the elements with atomic numbers 58–71 in the periodic table? *(4)*

● **10** The table below shows the groups, formulae and boiling temperatures of chlorides for the elements in Periods 2 and 3.

a) Explain why are there no entries in the table for Group 0. *(2)*

b) i) What pattern is shown by the formulae of the chlorides in Periods 2 and 3? *(2)*

ii) Suggest an explanation for the pattern you describe. *(4)*

c) The formulae OCl_2 and FCl are normally written as Cl_2O and ClF, respectively. Why is this? *(1)*

d) i) What is the pattern in the boiling temperatures of the chlorides of the elements in Periods 2 and 3? *(2)*

ii) Suggest an explanation for the pattern you describe. *(4)*

e) Phosphorus forms a second chloride, PCl_5, but nitrogen only forms the one chloride. Suggest a reason for this difference in terms of the electron configurations of the atoms of phosphorus and nitrogen. *(5)*

● **11** Discuss the following statements using examples to show the extent to which you think that they are true or false:

a) The atomic number of an element is a better guide to its atomic structure and is more useful in its classification than its relative atomic mass. *(6)*

b) The chemical properties of an element are largely determined by the number of electrons in the outer shell of its atoms. *(6)*

	Group						
	1	**2**	**3**	**4**	**5**	**6**	**7**
Period 2							
Formula of chloride	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2	FCl
Boiling temperature of chloride/°C	1340	520	13	77	71	4	−101
Period 3							
Formula of chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2	Cl_2
Boiling temperature of chloride/°C	1413	1412	423	58	76	136	−35

2 Bonding and structure

2.1 Investigating structure and bonding

The word 'structure' has different levels of meaning in science. On a grand scale, engineers design the structures of buildings and bridges; on the smallest scale, chemists and physicists explore the inner structure of atoms. Not surprisingly, scientists use different models and different theories to explain the structure and properties of materials at these different levels.

Scientists have developed increasingly sophisticated models to account for the structure, bonding and properties of materials as their knowledge has increased. No single model can be used to explain the properties of elements and compounds at all levels. Each has its advantages and its limitations and particular models are more appropriate in different contexts.

In this topic, crystal structures are best explained using Dalton's model of atoms and ions as discreet, tiny spheres. Metallic, ionic and covalent bonding are best explained using the model of electron shells.

The regular shapes of crystals suggest an underlying arrangement of the atoms, ions or molecules in their structure. Until the early part of the twentieth century, scientists could only guess at the arrangement of invisible atoms in crystals. Then, Sir Lawrence Bragg (1890–1971) realised that X-rays could be used to investigate crystal structures because their wavelengths are about the same as the distances between atoms in a crystal.

A narrow beam of X-rays is directed at a crystal of the substance being studied (Figure 2.1).

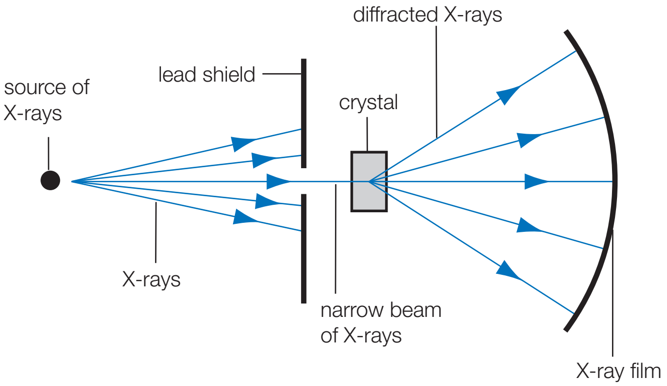


Figure 2.1 Using X-rays to study the structure of atoms or ions in a crystal.

The atoms or ions in the crystal scatter the X-rays producing a pattern of diffracted rays. The diffracted X-rays were originally photographed using X-ray film but can now be recorded electronically. From the diffraction pattern produced, such as that shown in Figure 2.2, it is possible to deduce the three-dimensional crystal structure by studying the pattern of dots.

Once the arrangement of the atoms or ions in a substance (the structure) is known – and also how they are held together (the bonding) – then the properties of a substance can be explained.

For example, copper is composed of closely packed atoms with freely moving outer electrons. These electrons move through the structure when copper is connected to a battery, so it is a good conductor of electricity. Atoms in the closely packed structure can slide over each other and because of this copper can be drawn into wires. These properties of copper lead to its use in electrical wires and cables.

Notice how:

- the structure and bonding of copper determine its properties
- the properties of copper determine its uses.

The links between structure, bonding and properties help to explain the uses of different materials. They explain why metals are used as conductors and why graphite is used in pencils.

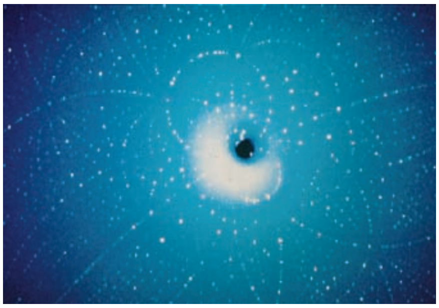


Figure 2.2 An X-ray diffraction pattern of lysozyme, a protein found in egg white. Data like this is now stored in the Worldwide Protein Data Bank, wwPDB.

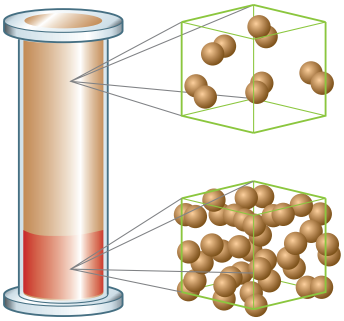


Figure 2.3 Molecules in bromine liquid and vapour. Many molecular elements and compounds are liquids or gases at room temperature because little energy is needed to overcome the weak forces between their molecules.

Two types of structure

Broadly speaking there are two types of structure – **giant structures** and **simple molecular structures**.

Materials with giant structures form crystals in which all the atoms or ions are linked by a network of strong bonding extending throughout the crystal. This strong bonding results in giant structures with high melting and boiling temperatures.

Substances with simple molecular structures consist of small groups of atoms. The covalent bonds linking the atoms in the molecules (intramolecular forces) are relatively strong, but the forces between molecules (**intermolecular forces**) are weak. These weak intermolecular forces allow the molecules to be separated easily. So molecular substances, such as bromine (Figure 2.3), have low melting and boiling temperatures.

Key terms

Giant structures are crystal structures in which all the atoms or ions are linked by a network of strong bonding extending throughout the crystal.

Simple molecular structures consist of groups of atoms held together by strong covalent bonding within the molecules, but with weak forces of attraction between the molecules.

Intermolecular forces are weak attractive forces between molecules.

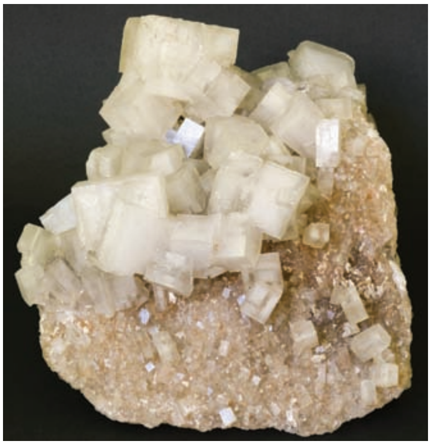


Figure 2.4 Crystals of rock salt (sodium chloride, NaCl).

Test yourself

1 a) The melting temperatures and boiling temperatures of selected elements are given in Table 2.1.

Use the data to decide whether they have giant or simple molecular structures.

b) Choose those elements from Question 1(a) where no covalent bonds are broken when the element melts.

Table 2.1 Melting temperatures and boiling temperatures of selected elements.

Element	Melting temperature/K	Boiling temperature/K
Boron	2573	2823
Fluorine	53	85
Silicon	1683	2628
Sulfur	386	718
Manganese	1517	2235
Iodine	387	457

2 Look at the crystals of rock salt in Figure 2.4.

a) What shape are most of the crystals of rock salt?

b) How do you think the ions are arranged in rock salt?

The main types of giant structures are ionic solids, giant covalent solids (these include ceramics and glasses, as well as diamond and graphite) and metals. All of these materials are solids that depend for their properties on three types of strong bonding – ionic bonding, covalent bonding and metallic bonding. Materials with specific properties can be chosen based on the type of bonding present. The pylons in Figure 2.5 contain metals which conduct electricity well and ceramics which don’t.

These three types of bonding – ionic, covalent and metallic – will be the main focus in the following sections of this topic. For each type of bonding, its strength depends on electrostatic attractions between positive and negative charges.

Figure 2.5 Metal cables in the electricity grid supported by steel pylons – a reminder that metals are strong, bendable and good conductors of electricity. Ceramic insulators between the conducting cables and the pylons prevent the electric current leaking away to earth.

2.2 Ionic bonding and structures

Atoms into ions

Compounds of metals with non-metals, such as sodium chloride and calcium oxide, are composed of ions. When compounds form between metals and non-metals, the metal atoms lose electrons and become positive ions (cations). At the same time, the non-metal atoms gain electrons and become negative ions (anions). For example, when sodium reacts with chlorine (Figure 2.6) each sodium atom loses its one outer electron to form a sodium ion, Na^+, which has the same electron structure as the noble gas neon. Chlorine atoms gain these electrons to form chloride ions, Cl^-, with the same electron configuration as the noble gas argon (Figure 2.7).

In many cases, when atoms react to form ions, they gain or lose electrons in such a way that the ions formed have the same electron configuration as a noble gas. This transfer of electrons involves redox (Section 3.2).

Chemists describe diagrams like that in Figure 2.7 as dot-and-cross diagrams, in which the electrons belonging to one reactant are shown as dots and those belonging to the other reactant are shown as crosses. But remember, all electrons are the same – dots and crosses are simply used to show which electrons come from the metal and which come from the non-metal. Dot-and-cross diagrams are useful because they provide a balance sheet for keeping track of the electrons when ionic compounds form.

Figure 2.8 shows simplified dot-and-cross diagrams for the formation of sodium chloride and calcium fluoride in which only the outer shell electrons are drawn.

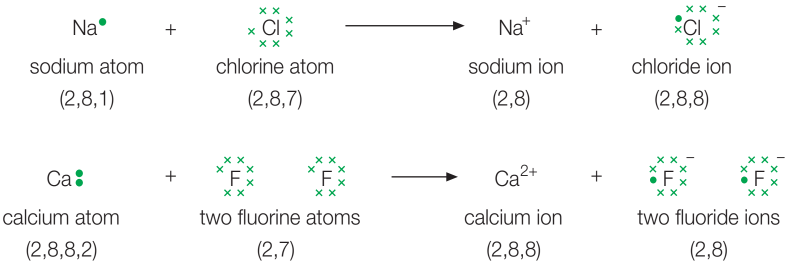


Figure 2.8 Dot-and-cross diagrams for the formation of sodium chloride and calcium fluoride showing only the electrons in the outer shells of the reacting atoms.

Figure 2.6 Hot sodium reacting with chlorine gas.

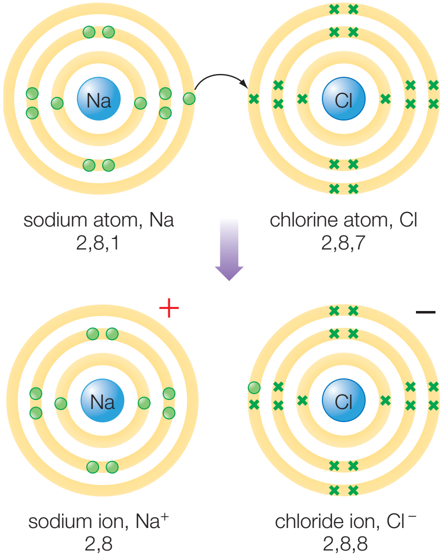


Figure 2.7 Formation of ions when sodium reacts with chlorine.

Test yourself

3 Draw dot-and-cross diagrams, showing only the outer electrons, for the ions present in:

a) lithium fluoride
b) magnesium chloride
c) lithium oxide
d) calcium sulfide.

4 With the help of a periodic table, predict the charges on ions of each of the following elements: caesium, strontium, gallium, selenium and astatine.

5 Why do metals form positive ions, while non-metals form negative ions?

Key terms

A **lattice** is a regular three-dimensional arrangement of atoms or ions in a crystal.

Ionic bonding refers to the strong electrostatic forces between oppositely charged ions in a lattice.

Ionic bonding

When metals react with non-metals, the ions produced form ionic crystals. An ionic crystal is a giant **lattice** containing billions of positive and negative ions packed together in a regular pattern.

Figure 2.9 shows how the ions are arranged in one layer of sodium chloride (NaCl) and Figure 2.10 shows a three-dimensional model of its structure.

In the lattice, each Na^+ ion is surrounded by Cl^- ions, and each Cl^- ion is surrounded by Na^+ ions. These oppositely charged ions attract each other. Chloride ions repel other nearby chloride ions and sodium ions repel other nearby sodium ions, but overall there are strong net electrostatic attractions between ions in all directions throughout the lattice. These electrostatic attractions between oppositely charged ions are described as **ionic bonding**.

Many other compounds have the same structure as sodium chloride including the chlorides, bromides and iodides of Li, Na, K and the oxides and sulfides of Mg, Ca, Sr and Ba.

The strength of the electrostatic attractions between ions depends on the charges of the ions and their radii. Ions with high charges and small radii produce the strongest electrostatic attractions. So, in general, a Group 2 compound has stronger ionic bonding with a higher melting temperature and lower solubility in water than a corresponding Group 1 compound.

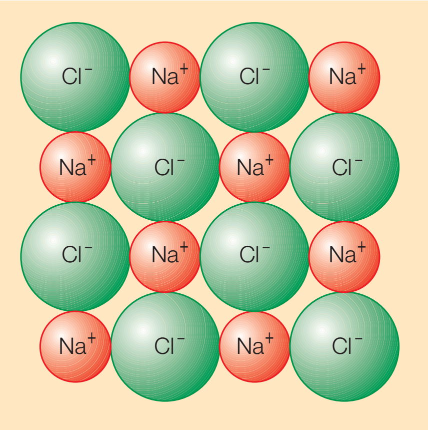


Figure 2.9 The arrangement of ions in one layer of a sodium chloride crystal.

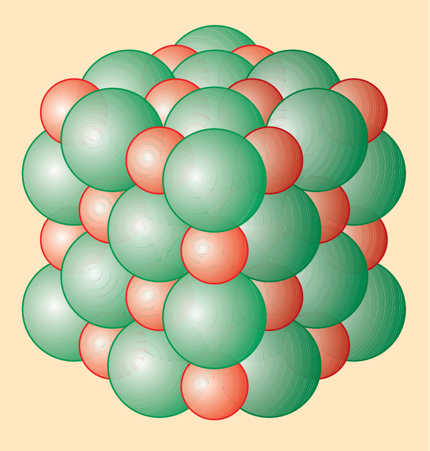


Figure 2.10 A three-dimensional model of the structure of sodium chloride. The smaller red balls represent Na^+ ions and the larger green balls represent Cl^- ions.

Tip

In mathematical terms, the size of the electrostatic force, F, between two charges is given by:

$$F \propto \frac{Q_1 \times Q_2}{d^2}$$

- The bigger the charges, Q_1 and Q_2, the stronger the force.
- The greater the distance, d, between the two charges, the smaller the force. This has a big effect because it is the square of the distance that affects the force.

Test yourself

6 Look carefully at Figures 2.9 and 2.10.

a) How many Cl^- ions surround one Na^+ ion in a layer of the NaCl crystal?

b) How many Cl^- ions surround one Na^+ ion in the three-dimensional crystal?

c) How many Na^+ ions surround one Cl^- ion in the three-dimensional crystal?

d) The structure of crystalline sodium chloride is described as 6 : 6 co-ordination. Why is this?

e) Use Figure 2.9 to explain that overall the attractive forces are stronger than the repulsive forces in an ionic crystal.

Properties of ionic compounds

Strong ionic bonding holds the ions firmly together in ionic compounds. This explains the properties of ionic compounds. They:

- are hard, brittle crystalline substances
- have high melting and boiling temperatures
- are often soluble in water and other polar solvents, but insoluble in non-polar solvents (Section 2.7)
- do not conduct electricity when solid, because their ions cannot move away from fixed positions in the giant lattice
- conduct electricity when they are melted or dissolved in water, because the charged ions are then free to move.

For example, when molten, sodium chloride conducts electricity. Ions from the **electrolyte** move towards the electrodes. Positive sodium ions move towards the negative terminal (cathode) while negative chloride ions move towards the positive terminal (anode). When the sodium ions reach the cathode, they gain electrons and become sodium atoms:

cathode (−): $2Na^+(l) + 2e^- \rightarrow 2Na(l)$

When chloride ions reach the anode, they lose electrons. The chlorine atoms formed then bond in pairs to become chlorine molecules:

anode (+): $2Cl^-(l) \rightarrow 2e^- + Cl_2(g)$

This process is described as **electrolysis**. It reverses the changes that happen when an ionic compound such as sodium chloride forms from its elements (Figure 2.6).

Tip

During electrolysis, positive ions gain electrons at the cathode; this is reduction. At the same time, electrons are lost at the anode; this is oxidation (see Chapter 3).

Key terms

Electrolysis is the decomposition of a compound by electricity. The compound which is decomposed is called an **electrolyte** and it is described as being electrolysed.

Tip

Electrolysis decomposes molten salts such as sodium chloride into their constituent elements. Electrolysis of salts in aqueous solution is more complicated. Elements such as oxygen (at the anode) or hydrogen (at the cathode) may be produced by the decomposition of water, rather than simple decomposition of the salt.

Migration of ions

The movement of ions can be observed during the electrolysis of coloured compounds. If a green solution of copper(II) chromate(VI) is electrolysed in a U-tube (Figure 2.11), the solution around the cathode turns blue and the solution around the anode turns yellow. This is because blue $Cu^{2+}(aq)$ cations are attracted by the negative cathode and migrate towards it. At the same time, yellow $CrO_4^{2-}(aq)$ ions are attracted by the positive anode and migrate towards it. This movement provides evidence for the existence of ions.

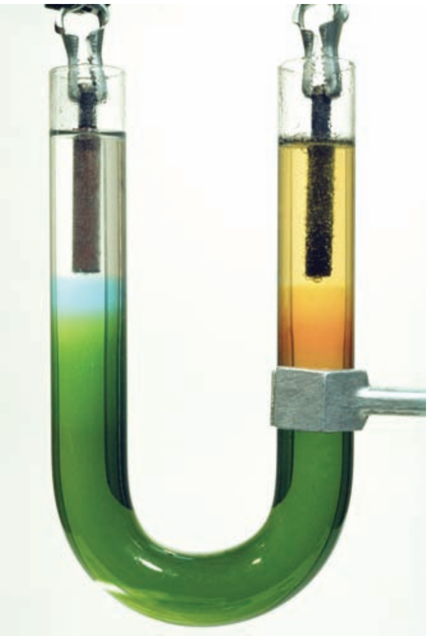


Figure 2.11 The migration of coloured ions during the electrolysis of copper(II) chromate(VI) solution.

Ionic radii

X-ray diffraction methods (Section 2.1) are used to study ionic compounds and to measure the spacing between ions in crystals. From the diffraction patterns, it is possible to calculate the radii of individual ions. The radius of the positive ion of an element is smaller than its atomic radius because it loses electrons from its outer shell when turning into an ion. The radius of the negative ion of an element is larger than its atomic radius because electrons are added to the outer shell (Figure 2.12).

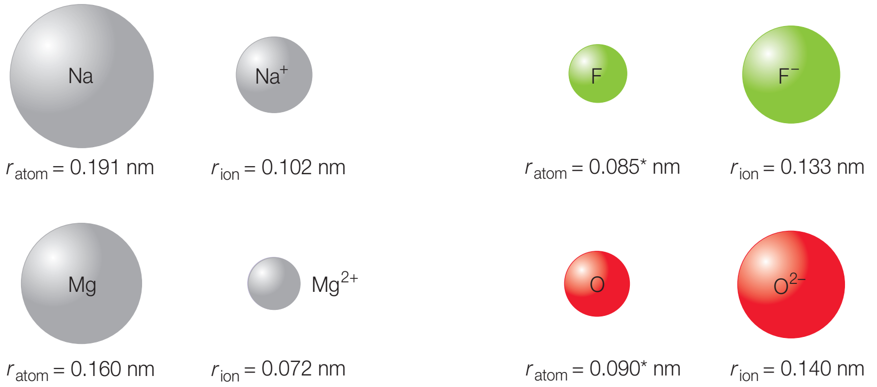


Figure 2.12 Comparing the radii of atoms and ions. (*The values for fluorine and oxygen atoms are estimates.)

Tip

- Atoms are neutral because the number of protons equals the number of electrons.
- Positive ions contain more protons than electrons; these cations are smaller than the neutral atom.
- Negative ions contain more electrons than protons; these anions are larger than the neutral atom.

Test yourself

7 The melting temperature of sodium fluoride is 993 °C, but that of magnesium oxide is 2852 °C.

  a) Write the formulae of these two compounds, showing charges on the ions.

  b) Suggest why the melting temperature of magnesium oxide is so much higher than that of sodium fluoride.

8 Write equations for the reactions at the cathode and anode during electrolysis of the following compounds:

  a) molten potassium bromide

  b) molten magnesium chloride.

9 A strip of wet filter paper is placed on a microscope slide and a small crystal of potassium manganate(VII) is placed at the centre of the paper. Leads from a 40 V DC power supply are attached to the ends of the filter paper and the power supply is switched on. After 30 minutes a purple colour is seen to have spread towards the positive terminal.

Explain the movement of the purple colour.

Activity

Identifying and explaining the trends in ionic radii

Table 2.2 shows the radii of ions of the elements in Group 1, and those of the consecutive elements from nitrogen to aluminium in the periodic table.

Look carefully at the data in Table 2.2.

1 Describe and explain the trend in ionic radii in Group 1 of the periodic table.

2 Do you think this trend is repeated in other groups of the periodic table? State 'yes' or 'no' and explain your answer.

3 Use the s, p, d, f notation to describe the electron configuration of:
- **a)** a nitride ion, N^{3-}
- **b)** a fluoride ion, F^-
- **c)** a sodium ion, Na^+
- **d)** an aluminium ion, Al^{3+}.

4 **a)** All the ions of consecutive elements in the periodic table from N^{3-} to Al^{3+} are described as 'isoelectronic'. What do you think this means?
- **b)** Describe the trend in ionic radii for the isoelectronic ions from N^{3-} to Al^{3+}.
- **c)** Explain the trend in ionic radii for the isoelectronic ions from N^{3-} to Al^{3+}.

Table 2.2 Ionic radii.

Ions of Group 1	Li^+	Na^+	K^+	Rb^+	Cs^+	
Radius/nm	0.074	0.102	0.138	0.149	0.170	
Ions of N to Al	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
Radius/nm	0.171	0.140	0.133	0.102	0.072	0.053

2.3 Covalent bonding and structures

Ionic bonding always produces giant structures of ionic lattices. Ionic compounds are, therefore, always solids at room temperature.

Covalent bonding can also produce giant structures, called giant covalent lattices, but can also lead to simple molecular structures.

A **covalent bond** forms when atoms share electrons – a single covalent bond consists of a shared pair of electrons.

The atoms are held together by the strong electrostatic attraction between the positive charges on their nuclei and the negative charge on the shared electrons.

The electron configuration of fluorine is $1s^22s^22p^5$ or more simply 2, 7, with seven electrons in the outer shell. When two fluorine atoms combine to form a molecule, they share a pair of electrons, one provided by each fluorine atom. The electron configuration of each atom in the molecule is then like that of neon, the nearest noble gas (Figure 2.13).

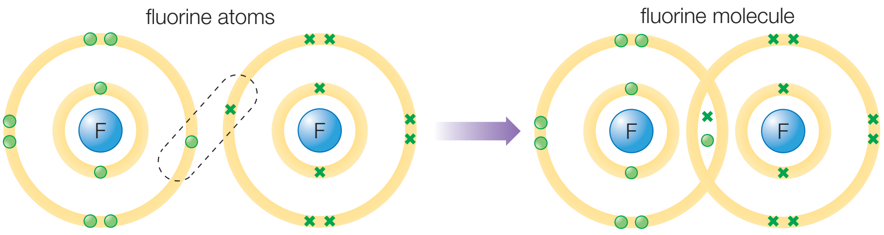


Figure 2.13 Covalent bonding in a fluorine molecule.

Key term

A **covalent bond** is the strong electrostatic attraction between two nuclei and the shared pair of electrons between them.

Tip

Metallic bonding also involves the sharing of electrons but, whereas the electrons in metals are delocalised and can move throughout the lattice, the electron pair shared in a covalent bond is fixed in position between the two nuclei. These electrons are 'localised'.

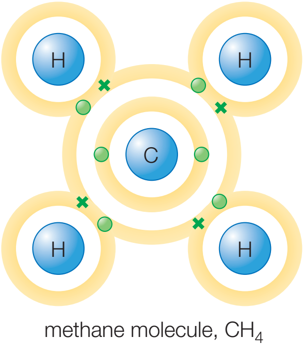


Figure 2.14 Covalent bonding in methane.

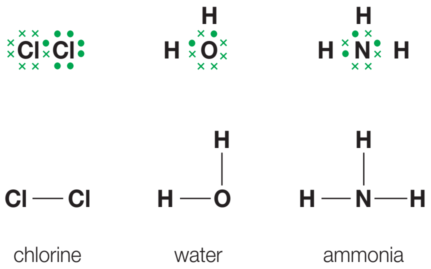


Figure 2.15 Covalent bonds in three molecules shown both as dot-and-cross diagrams and by using lines between the symbols.

Covalent bonds also link the atoms in non-metal compounds. Figure 2.14 shows the covalent bonding in methane.

Dot-and-cross diagrams, showing only the electrons in outer shells, provide a simple way of representing covalent bonding. An even simpler way of showing the bonding in molecules represents each covalent bond as a line between two symbols. So, chemists write a fluorine molecule as F–F. This is the structural formula, showing atoms and bonding. The molecular formula of fluorine is F_2. Three examples of both methods are shown in Figure 2.15.

Tip

The number of covalent bonds formed by a non-metal atom in Period 2 can be predicted from its place in the periodic table. An atom of fluorine (Group 7) has one electron fewer than a noble gas so it forms one covalent bond. An atom of oxygen (Group 6) has two electrons fewer than a noble gas so it forms two covalent bonds. An atom of nitrogen (Group 5) has three electrons fewer than a noble gas so it forms three covalent bonds. An atom of carbon (Group 4) has four electrons fewer than a noble gas so it forms four covalent bonds. Note that this only applies to the elements in Period 2; the situation for the elements in Period 3 and beyond is more complex.

Multiple bonds

One shared pair of electrons makes a single bond. Double bonds and triple bonds are also possible with two or three shared pairs, respectively.

There is a double bond between the two oxygen atoms in an oxygen molecule, and double bonds between both the oxygen atoms and the carbon atom in carbon dioxide (Figure 2.16). With two electron pairs involved in the bonding, there is a region of high electron density between the two atoms joined by a double bond. Figure 2.17 shows two molecules which each contain a triple bond.

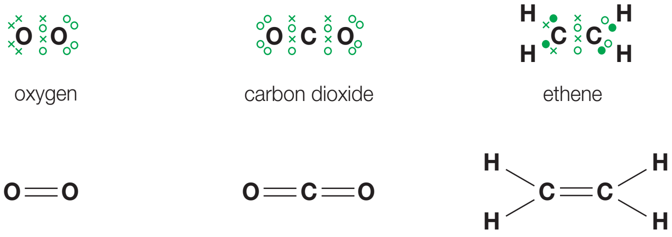


Figure 2.16 Three molecules with double covalent bonds.

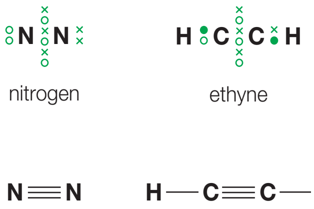


Figure 2.17 Two molecules with triple covalent bonds.

Tip

The carbon–carbon double bond in alkenes is considered in more detail in Section 6.2.7.

Lone pairs of electrons

In many molecules, there are atoms with outer shells that contain pairs of electrons which are not involved in the bonding between atoms in the molecule. Chemists call these **lone pairs** of electrons (Figure 2.18).

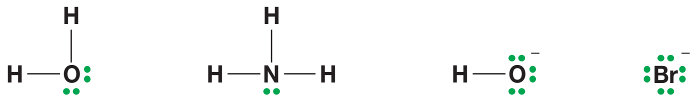


Figure 2.18 Molecules and ions with lone pairs of electrons.

Lone pairs of electrons:

- affect the shapes of molecules (Section 2.4)
- are used to form **dative covalent bonds**
- are important in the chemical reactions of some compounds including water and ammonia.

Key terms

A **lone pair** of electrons is pair of electrons in the outer shell of one of the atoms in a molecule or ion which is not involved in bonding.

A **dative covalent bond** is a bond in which two atoms share a pair of electrons, both the electrons being donated by one atom.

Dative covalent bonds

In a covalent bond, two atoms share a pair of electrons and each atom supplies one electron to make up the pair. Sometimes, however, one atom provides both the electrons and chemists call this a dative covalent bond. The word 'dative' means 'giving' and one atom gives both the electrons to make the covalent bond. The other atom accepts the electron pair into a vacant orbital. Once formed, there is no difference between a dative covalent bond and any other covalent bond. An alternative name for a dative covalent bond is a co-ordinate bond.

An ammonia molecule has a lone pair and a hydrogen ion has a vacant 1s orbital. A dative covalent bond is formed when ammonia reacts with a hydrogen ion to make an ammonium ion, NH_4^+ (Figure 2.19). A dative bond is represented by an arrow in displayed formulae like that of NH_4^+. The arrow points from the atom donating the electron pair to the atom receiving them (Figure 2.19).

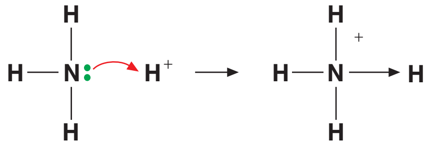


Figure 2.19 Formation of an ammonium ion, NH_4^+.

Dative covalent bonding also accounts for the structure of Al_2Cl_6 molecules. When solid aluminium chloride is heated, it sublimes (turns straight to vapour) and Al_2Cl_6 molecules are formed. These molecules contain two dative covalent bonds formed when a lone pair on a chlorine atom is donated into the empty orbital on an aluminium atom (Figure 2.20).

At higher temperatures these double molecules (dimers) split into $AlCl_3$ molecules.

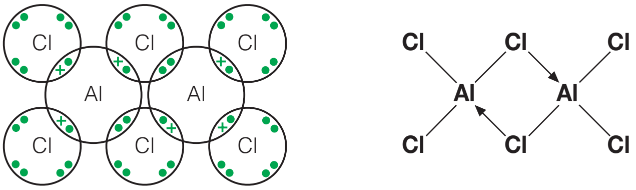
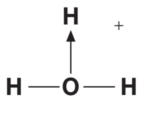


Figure 2.20 An Al_2Cl_6 molecule shown as a dot-and-cross diagram and also using arrows to represent the dative covalent bonds.

Tip

When an acid dissolves in water, aqueous hydrogen ions called oxonium ions are formed. A lone pair of electrons on a water molecule forms a dative covalent bond with a hydrogen ion from an acid. The formula of the oxonium ion is H_3O^+. It is often convenient to write $H^+(aq)$ instead, but remember that the hydrogen ion is hydrated.



oxonium ion

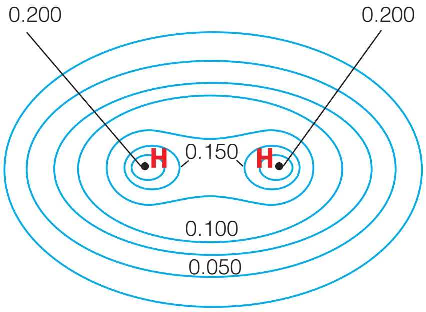


Figure 2.21 An electron density map for hydrogen, H_2. The units for the contours are electrons per 10^{-30} m^3.

Test yourself

10 Look at the electron density map of hydrogen, H_2, in Figure 2.21.
- **a)** What kind of bond exists between the hydrogen atoms in a hydrogen molecule?
- **b)** What evidence does the electron density map provide for the existence of a bond between the hydrogen atoms in a hydrogen molecule?

11 Draw dot-and-cross diagrams showing all the electrons in:
- **a)** hydrogen chloride, HCl
- **b)** ammonia, NH_3.
- **c)** ammoniaum ion, NH_4^+.

12 Draw dot-and-cross diagrams using only the outer shell electrons and also draw lines between symbols to show the covalent bonding in:
- **a)** hydrogen sulfide, H_2S
- **b)** ethane, C_2H_6
- **c)** carbon disulfide, CS_2
- **d)** nitrogen trifluoride, NF_3
- **e)** phosphine, PH_3.

13 Identify the atoms with lone pairs of electrons in the following molecules and state the number of lone pairs:
- **a)** ammonia
- **b)** water
- **c)** hydrogen fluoride
- **d)** carbon dioxide.

14
- **a)** In aqueous solution, acids donate H^+ ions to water molecules forming H_3O^+ ions. Draw a dot-and-cross diagram to show the formation of an H_3O^+ ion.
- **b)** Boron fluoride forms molecules with the formula BF_3. Draw a dot-and-cross diagram for BF_3 and then explain why BF_3 molecules readily react with other molecules.

Key term

Bond length is defined as the distance between the nuclei of two bonded atoms in a molecule.

Bond length and bond strength

X-ray diffraction studies (Section 2.1) enable chemists to investigate structures and to measure **bond lengths** in covalent substances in the solid phase. Microwave spectroscopy can be used to obtain values for bond lengths in molecules in the vapour phase.

Bond length depends both on the size of the atoms involved and the number of pairs of electrons shared (see Table 2.3).

Larger atoms form longer bonds because larger atoms have more electrons which shield the nuclei and reduce the attraction for the electron cloud. For instance, the length of the bond between hydrogen and the halogen atoms increases down the group as the halogen atoms get larger.

Single bonds are longer than double bonds, which are longer than triple bonds. The nuclei can remain closer together if the shared electron cloud contains more electrons to overcome the repulsion of the nuclei.

The carbon–carbon single bond consists of one shared pair of electrons and is longer than the carbon–carbon double bond which involves two shared pairs. The triple bond in which three pairs are shared is shorter still. The values for the carbon–carbon bonds in Table 2.3 are averages as these bonds occur in many different compounds.

The strength of a bond varies inversely with its length. A short bond is stronger with a greater **bond energy**.

Bond energies are discussed in more detail in Section 8.7.

Table 2.3 Some bond lengths and bond energies.

Bond	Bond length/ nm	Bond energy/ kJ mol^{-1}
H–F	0.092	568
H–Cl	0.127	432
H–Br	0.141	366
H–I	0.161	298
C–C	0.154	347
C=C	0.134	612
C≡C	0.120	838

Key term

The **bond energy** of a particular bond is the energy required to break one mole of the bonds in a substance in the gaseous state.

Simple molecular structures

In most non-metal elements, atoms are joined together in small molecules such as hydrogen (H_2), nitrogen (N_2), phosphorus (P_4), sulfur (S_8) and chlorine (Cl_2).

Most of the compounds of non-metals with other non-metals also have simple molecular structures. This is true of simple compounds such as water, carbon dioxide, ammonia, methane and hydrogen chloride. It is also true of the many thousands of carbon compounds (see Chapter 6.1).

The covalent bonds holding atoms together within these simple molecular structures are strong, so the molecules do not break up into atoms easily. However, the forces between the individual molecules (intermolecular forces) are weak, so it is quite easy to separate them. This means that molecular substances are often liquids or gases at room temperature and that molecular solids are usually easy to melt and evaporate (Figure 2.22).

Some non-metal elements including diamond and some compounds of non-metals including silicon dioxide consist of giant structures of atoms held together by covalent bonding. These substances are hard and have high melting temperatures because the covalent bonds are strong. Giant covalent structures are considered in Section 2.8.

Tip

Energy is needed to break bonds and energy is given out when bonds form.

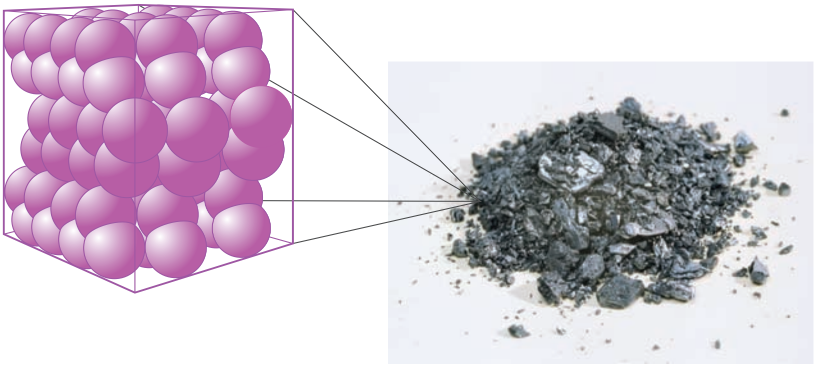


Figure 2.22 The structure of iodine showing the arrangement of I_2 molecules. The forces between I_2 molecules are so weak that iodine changes directly from solid to vapour on only gentle warming; it sublimes easily.

Properties of simple molecular substances

In general, simple molecular substances, whether elements or compounds:

- are usually gases, liquids or soft solids at room temperature
- have relatively low melting and boiling temperatures
- do not conduct electricity as solids, liquids or gases because they contain neither ions nor free electrons to carry the electric charge
- are usually more soluble in non-polar solvents (see Section 2.7), such as hexane, than in water – and the solutions in hexane do not conduct electricity.

Tip

Some molecular substances dissolve in water and react with it to form ions, so the 'solution' in water does conduct electricity. For example, molecules of hydrogen chloride dissolve in water and react with it to form H^+(aq) and Cl^-(aq) ions. The solution is known as hydrochloric acid and conducts electricity because of the ions present.

Tip

Ionic and covalent bonding both depend on electrostatic attractions to hold the ions and atoms together. But, whereas the electrostatic attraction by an ion is the same in all directions, a covalent bond between two atoms is directional.

Test yourself

15 Look at the structure of iodine shown in Figure 2.22. Describe the arrangement of the molecules in solid iodine.

16 The Cl–Cl and Br–Br bond lengths are 0.199 nm and 0.228 nm respectively.

a) Explain why the Br–Br bond is longer.

b) State which of these two bonds has the higher bond energy and explain your answer.

17 Explain why the O=O bond is shorter and stronger than the O–O bond.

2.4 The shapes of molecules and ions

Electron-pair repulsion theory

Key term

A **bond angle** is the angle between two covalent bonds in a molecule or giant covalent structure.

X-ray diffraction studies provide very accurate evidence not only about bond lengths but also about **bond angles** in molecules and in ions such as NH_4^+ which have covalent bonds. The results show that covalent bonds have a definite direction and a definite length. For example, X-ray diffraction studies show that all the C–H bond lengths in methane, CH_4, are 0.109 nm and all the H–C–H bond angles are 109.5° (Figure 2.23).

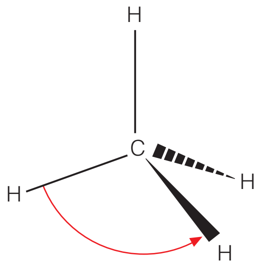


Figure 2.23 All the bond angles in methane are 109.5° and all the C–H bond lengths are 0.109 nm.

Tip

In 3D structures, such as methane in Figure 2.23, the two normal lines represent covalent bonds in the plane of the paper. The solid wedge represents a bond coming out of the paper towards the reader, while the hashed bond represents a bond going into the paper away from the reader.

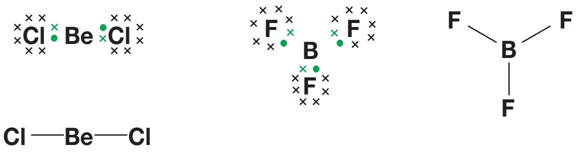
Drawing 3D structures is difficult, so molecules are often represented with normal line bonds but still with an attempt at a 3D representation. See the methane structure in Table 2.4. Section A1.8 in Appendix A1 discusses this further.

Chemists have developed a very simple theory to explain and predict the shapes and bond angles of simple molecules and ions containing covalently bonded atoms. The theory is based on the repulsion of electron pairs in the outermost shell of the central atom. It is called the electron-pair repulsion theory. The theory says that electron pairs in the outer shell of atoms and ions repel each other and get as far apart as possible.

If a methane molecule was shaped as a flat cross, the angle between carbon–hydrogen bonds would be 90°. By adopting the three-dimensional shape known as a tetrahedron, shown in Figure 2.23, the bond angle increases to 109.5°, so there is maximum separation and therefore minimum repulsion between the pairs of electrons. Consider the molecules of beryllium chloride and boron trifluoride in Figure 2.24. In the $BeCl_2$ molecule, beryllium has only two pairs of electrons in its outer shell. In order to get as far apart as possible, these two pairs of electrons must be on opposite sides of the beryllium atom. The shape of the molecule is described as linear and the Cl–Be–Cl bond angle is 180°.

Tip

Sometimes the abbreviation VSEPR is used for the electron-pair repulsion theory. This is short for 'valence shell electron-pair repulsion'. The valence shell of an atom is its outer shell.



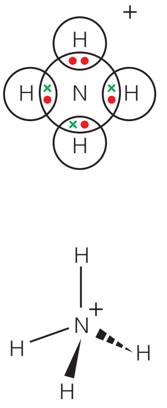
linear

trigonal planar

Figure 2.24 The shapes of molecules with two and three electron pairs around the central atom.

The next simplest example of the electron-pair repulsion theory is shown by boron trifluoride, BF_3. In the BF_3 molecule, boron has three electron pairs in its outer shell. This time, to get as far apart as possible, the three pairs must occupy the corners of a triangle around the boron atom. The shape of this molecule is described as trigonal planar and the F–B–F bond angles are 120°.

Now consider the ammonium ion, NH_4^+, in Figure 2.25. In this ion, nitrogen has four electron pairs in its outer shell, each bonded to a hydrogen atom. These electron pairs repel each other and get as far apart as possible. The four hydrogen atoms are, therefore, at the corners of a tetrahedron. All the H–N–H bond angles are 109.5° and the shape of the NH_4^+ ion is tetrahedral, exactly the same as methane.



tetrahedral

Figure 2.25 The shape of the NH_4^+ ion.

The methane molecule, CH_4, and the ammonium ion NH_4^+ have exactly the same number and arrangement of electrons; they are said to be **isoelectronic**.

Key term

Isoelectronic molecules and ions have exactly the same number and arrangement of electrons.

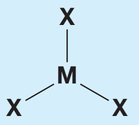
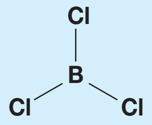
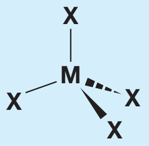
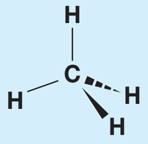
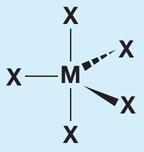
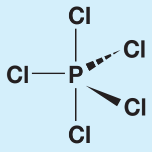
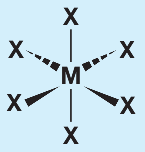
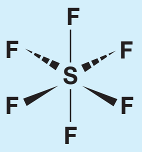
Table 2.4 summarises the shapes of molecules with two, three, four, five and six pairs of electrons, based on the electron-pair repulsion theory. In each case, the electron pairs are repelled as far apart as possible. The table also shows the predicted bond angles for each molecule.

The electron-pair repulsion theory shows how chemists can make generalisations from their results and use these generalisations to make predictions.

Tip

Ions and molecules which are isoelectronic have exactly the same shape.

Table 2.4 The shapes of molecules with two to six pairs of bonding electrons around the central atom.

Number of electron pairs	Shape	Description	Bond angle XMX	Example of molecule in gas phase	
2	X—M—X	Linear	180°	$BeCl_2$	Cl—Be—Cl
3		Trigonal planar	120°	BCl_3	
4		Tetrahedral	109.5°	CH_4	
5		Trigonal bipyramid (two triangle-based pyramids base to base)	90°, 120° and 180°	PCl_5	
6		Octahedral (two square-based pyramids base to base)	90° and 180°	SF_6	

Tip

The elements in Period 2 only have 2s and 2p orbitals available for bonding. The maximum number of electrons these orbitals can contain is eight in four pairs, so no Period 2 element can form more than four bonds. This eight-electron maximum is sometimes called the octet rule.

Elements in Period 3 and beyond also have d orbitals available for bonding. Together with s and p orbitals these d orbitals allow more than four bonds to be formed. So elements after Period 2 are not constrained by the octet rule.

Tip

Learn the five basic shapes and bond angles shown in Table 2.4. For simplicity, the bonds may all be drawn as single lines (see Appendix A1.8, page 300).

Test yourself

18 Why are covalent bonds described as 'directional bonds'?

19 Draw dot-and-cross diagrams of the following simple molecules, showing only electrons in the outer shell of all atoms.

a) PF_5 **b)** $SiCl_4$ **c)** BCl_3

20 Predict the shape and bond angle in the following molecules.

a) PF_5 **b)** $SiCl_4$ **c)** BCl_3

21 Draw dot-and-cross diagrams of the following ions, then predict the shape and give the bond angles.

a) PH_4^+ **b)** BH_4^- **c)** PF_6^-

Molecules and ions with lone pairs and multiple bonds

Lone pairs

Some molecules, such as ammonia and water, contain non-bonding pairs (or lone pairs) of electrons as well as bonding pairs (Figure 2.26).

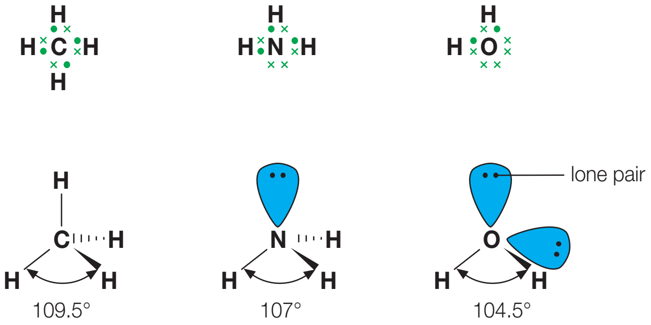


Figure 2.26 Shapes and bond angles in molecules with bonding pairs and lone pairs of electrons.

Tip

Learn the shapes and bond angles shown in Figure 2.26. Each extra lone pair reduces the bond angle by about 2.5°.

Ammonia and water are isoelectronic with methane. All have four pairs of electrons in the outer shell of the central atom (see dot-and-cross diagrams in Figure 2.26).

In methane, all four pairs of electrons are bonding pairs between the central carbon atom and a hydrogen atom. In ammonia, three of the four pairs make up N−H bonds as bonding pairs, but the fourth is a lone pair. Each of these four electron pairs repels the others, so they form a tetrahedral shape around the nitrogen atom. But the positions of the *atoms* in the NH_3 molecule make a shape which is pyramidal – a triangle-based pyramid – with a nitrogen atom at the top and hydrogen atoms at the three corners of its base.

In water, there are also four pairs of electrons around the central atom – two bonding pairs and two lone pairs. The shape formed by these electron pairs is tetrahedral again, but the shape of the water molecule, H−O−H, is described as V-shaped or bent.

Lone pairs of electrons are held closer to the central atom than the bonding pairs. This means that they have a stronger repelling effect than bonding pairs. Therefore, the strength of repulsion between electron pairs is:

lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair

This explains why the bond angle in ammonia, with one lone pair, is less than that in methane; and why the bond angle in water, with two lone pairs, is less than that in ammonia.

Similar predictions about shapes and bond angles can be made for ions such as H_3O^+, BF_4^- and NH_2^- (Figure 2.27).

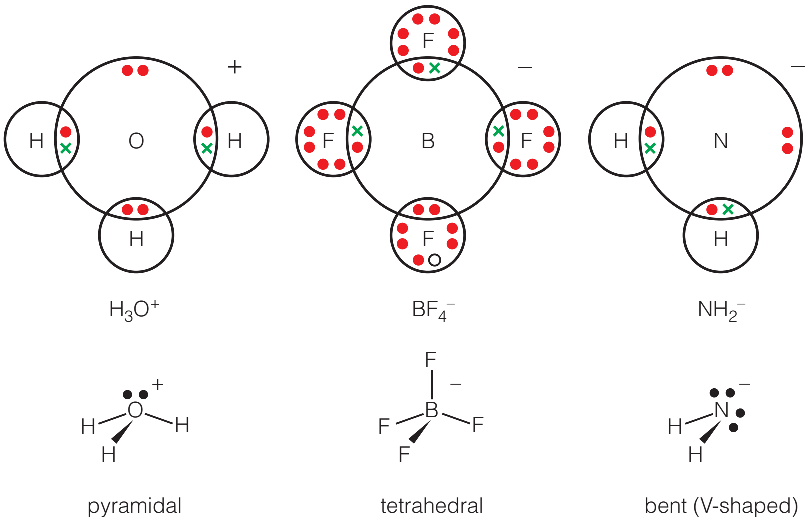


Figure 2.27 Dot-and-cross diagrams and shapes of some ions.

Test yourself

22 Draw dot-and-cross diagrams of the following species, then predict the shape and give the bond angles.

a) PH_3	**b)** SF_4
c) ICl_2^-	**d)** XeF_2

23 a) Draw a dot-and-cross diagram of the molecule SiH_4, then predict the shape and give the bond angle.

b) Write the formulae of two ions that are isoelectronic with SiH_4.

Multiple bonds

The arrangement of the electrons in double bonds and triple bonds is considered in more detail in Section 6.2.7. However, when it comes to predicting molecular shapes, double bonds and triple bonds count as just one centre of negative charge (electron-pair repulsion axis) and affect the shapes of molecules and ions in a similar way to electrons in single bonds. So all of these (single bonds, lone pairs, double bonds and triple bonds) can be regarded as separate centres of negative charge when predicting the overall shapes of molecules and ions (Figure 2.28).

Tip

As a double bond is a greater centre of electron density than a single bond, there is slightly greater repulsion of other bonding pairs by the electrons in double bonds than by those in single bonds. This increases the bond angles around the double bond. For instance, the H–C–O bond angle in methanal (Figure 2.28) is found to be 121° rather than the expected 120° in trigonal planar molecules such as BCl_3.

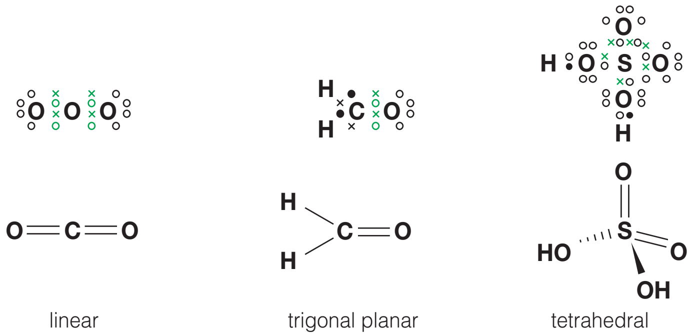


Figure 2.28 The shapes of some molecules with multiple bonds: carbon dioxide, CO_2; methanal, H_2CO; and sulfuric acid, H_2SO_4.

Test yourself

24 Draw dot-and-cross diagrams for the following molecules and ion and predict their shapes.

a) HCN **b)** N_2

c) SO_2 **d)** SO_4^{2-}

25 a) Draw a dot-and-cross diagram for CH_3Cl.

b) What is the shape of the CH_3Cl molecule?

c) The H–C–H bond angles in CH_3Cl are 111°, whereas the Cl–C–H bond angles are 108°.

Why do you think the Cl–C–H bond angles are smaller than the H–C–H bond angles? (Hint: The C–H bond is much shorter than the C–Cl bond.)

2.5 Polar bonds and polar molecules

A spectrum of bonding

The electron pair in a covalent bond is shared equally if the two atoms joined by the bond are the same. The bonding is purely covalent. However, the electron pair in a covalent bond is not shared equally if the two atoms joined by the bond are different. The nucleus of one atom attracts the electrons more strongly than the nucleus of the other. This means that one end of the bond has a slight excess of negative charge. This excess is represented by the symbol δ−. At the other end of the bond, the electrons are less strongly attracted and the charge cloud of electrons does not cancel the positive charge on the nucleus. This end of the bond has a partial positive charge (δ+).

The bonding is covalent but the **polar covalent bond** has some separation of charge (Figure 2.29).

Key term

Polar covalent bonds are bonds between atoms of different elements. The shared electrons are drawn towards the atom with the stronger pull on the electrons. The bonds have a positive pole at one end and a negative pole at the other.

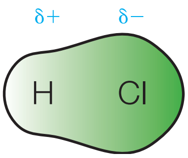


Figure 2.29 A polar covalent bond in hydrogen chloride. Overall the molecule is uncharged – it is not an ion – but the uneven distribution of electrons leads to partial charges at the ends of the covalent bond.

Compounds such as potassium fluoride and sodium chloride exist as giant lattices of spherical ions held together by electrostatic forces. This bonding is purely ionic. However, in ionic compounds where the cations are small and highly charged, these cations distort the electron clouds of the anions in a process called polarisation. This leads to an increase in the electron density in the space between the ions, some sharing of electrons and partial covalency. Polarisation is considered in more detail in Section 4.7 where the thermal stability of Group 1 and 2 carbonates and nitrates is discussed.

Tip

The δ symbol is the Greek letter 'delta'. Chemists use this symbol for a small quantity or change. They use the symbols δ+ and δ− for the small charges at the ends of a polar bond. They use the capital Greek 'delta', Δ, for larger changes or differences.

So the bonding in many compounds is neither purely ionic nor purely covalent but lies somewhere on a bonding spectrum between these two extremes (Figure 2.30).

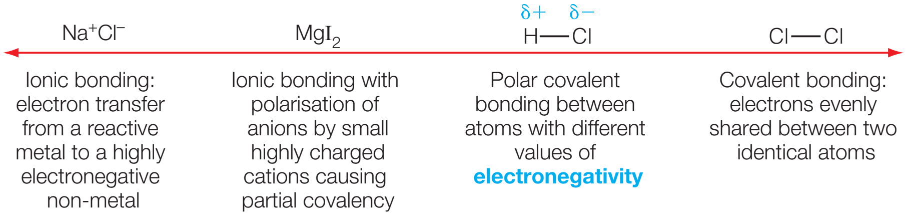

Na^+Cl^-
MgI_2
$\delta+$ $\delta-$
H—Cl
Cl—Cl
Ionic bonding: electron transfer from a reactive metal to a highly electronegative non-metal
Ionic bonding with polarisation of anions by small highly charged cations causing partial covalency
Polar covalent bonding between atoms with different values of **electronegativity**
Covalent bonding: electrons evenly shared between two identical atoms

Figure 2.30 A bonding spectrum from purely ionic to purely covalent.

Key term

Electronegativity is the ability of an atom to attract the bonding electrons in a covalent bond. In a polar bond, the shared electrons are drawn towards the more electronegative atom.

Electronegativity

Chemists use electronegativity values to predict the extent to which the bonds between different atoms are polar. The stronger the pull of an atom on the electrons it shares with other atoms, the higher its electronegativity. Oxygen is more electronegative than hydrogen, so an O−H bond is polar with a slight negative charge on the oxygen atom and a slight positive charge on the hydrogen atom.

There are several scales of electronegativity which reflect the changes in electronegativity in the periodic table (Figure 2.31), but that devised by Linus Pauling (1901–1994) is the most commonly used. Pauling assigned values on a scale from 0 to 4, with fluorine, the most electronegative element, given the value 4.0.

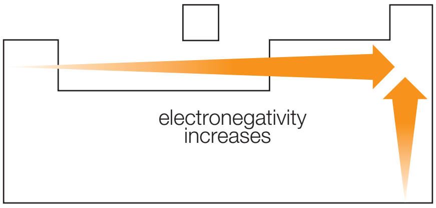

electronegativity increases

Figure 2.31 Trends in electronegativity for s- and p-block elements.

Electronegativity is used to compare one element with another qualitatively, so when comparing elements it is enough to know the trends in electronegativity values across and down the periodic table.

Highly electronegative elements, such as fluorine and oxygen, are at the top right of the periodic table. The least electronegative elements, such as caesium, are at the bottom left.

Electronegativity increases across a period. The nuclear charge increases but the number of shielding electrons remains constant, so the attraction for the shared electron pair increases.

Electronegativity decreases down a group. Although the nuclear charge increases, there is an increase in the number of shielding electrons and the shared electron pair is further from the nucleus so is attracted less strongly.

The bigger the difference in the electronegativity of the elements forming a bond, the more polar, and possibly more ionic, the bond. The bonding in a compound becomes ionic when the difference in electronegativity is large enough for the more electronegative element to remove electrons completely from the other element. This happens in compounds such as sodium chloride, magnesium oxide and calcium fluoride.

Activity

Interpreting electronegativity values

The version of the periodic table in Table 2.5 shows Pauling electronegativity values for selected elements.

1 Why are electronegativity values for He and Ne not included in the table?

2 Identify two elements in the table that would combine to form a compound with covalent bonds that are not polar.

3 Identify the two elements in the table that would form the most purely ionic compound.

4 What is the trend in the values of electronegativity from left to right across a period?

5 **a)** Draw diagrams showing the electrons in the main shells for lithium and fluorine.

b) Use your diagrams and the concept of shielding to explain why fluorine is much more electronegative than lithium.

6 What is the trend in the values of electronegativity down a group?

7 **a)** Draw diagrams showing the electrons in the main shells for fluorine and chlorine.

b) Use your diagrams and the concept of shielding to explain why fluorine is more electronegative than chlorine.

Table 2.5 Pauling electronegativity values.

		H 2.1					
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0					Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0					I 2.5	Xe 2.6

Test yourself

26 **a)** Use Figure 2.31 and the electronegativity values in Table 2.5 to predict the polarity of the bonds in these molecules: H_2S, NO, CCl_4, ICl.

b) Put these bonds in order of polarity, with the most polar first: C–I, C–H, C–Cl, C–O, C–F, C–Br.

27 Put these sets of compounds in order of the character of the bonding, with the most ionic on the left and the most covalent on the right:

a) Al_2O_3, Na_2O, MgO, SiO_2 **b)** LiI, NaI, KI, CsI.

28 Iron(III) chloride can be prepared by passing dry chlorine over hot iron. The iron(III) chloride sublimes away from the metal surface and can be collected where the vapour solidifies on a cold surface.

Iron(II) chloride does not sublime and cannot be prepared in this way.

a) Write an equation for this preparation of iron(III) chloride.

b) Explain why iron(III) chloride easily turns to vapour despite being a metal compound.

c) Explain why iron(II) chloride does not sublime in the same way.

29 The ionic model of bonding involves the transfer of electrons from metals to non-metals to form oppositely charged ions held together by strong electrostatic forces.

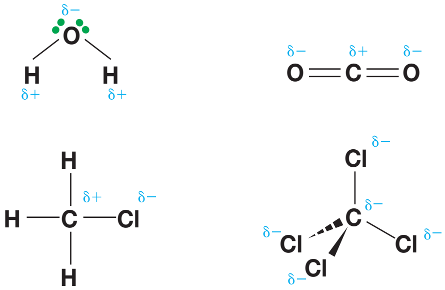
Discuss the strengths and weaknesses of this model in explaining the properties of metal compounds.

Key term

Polar molecules contain polar bonds which do not cancel each other out, so that the whole molecule is polar.

Polar molecules

The covalent bonds in hydrogen chloride are polar and, as there is only one bond in each molecule, overall these are **polar molecules**. There are, however, molecules with polar bonds that are not polar overall. One example is the tetrahedral molecule tetrachloromethane (Figure 2.32). The four polar bonds in CCl_4 are arranged symmetrically around the central carbon atom so that overall they cancel each other out.



overall polar

overall non-polar

Figure 2.32 Molecules with polar bonds. Note that in the examples on the left, the net effect of all the polar bonds is a polar molecule; in the examples on the right the overall effect is a non-polar molecule.

Tip

Make sure you consider the three-dimensional structure of a molecule when working out whether it has an overall dipole. A flat representation of dichloromethane could suggest that the effect of the two polar bonds cancel, but the 3D structure shows that this is not the case and the molecule has an overall dipole (Figure 2.33).

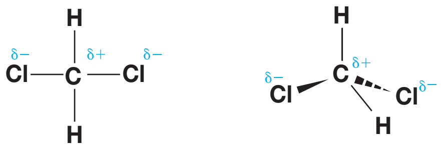


Figure 2.33 In the left-hand flat representation, the polar bonds are drawn opposite to each other, so it appears that their effects would cancel. In the right-hand 3D representation, the bonds are shown correctly 109.5° apart in the tetrahedral molecule. So the molecule does have an overall dipole.

Polar molecules are little electrical dipoles – they have a positive electric pole and a negative electric pole. These two poles of opposite charge in a molecule are called dipoles. Dipoles tend to line up in an electric field (Figure 2.34).

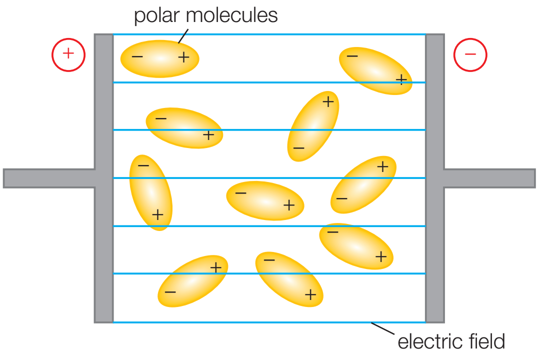


Figure 2.34 Polar molecules in an electric field. The electrostatic forces tend to line up the molecules with the field. Random movements due to the kinetic energy of the molecules tend to disrupt the alignment of the molecules.

The bigger the dipole, the bigger the twisting effect – or dipole moment – on a molecule in an electric field. By making measurements with a polar substance between two electrodes it is possible to calculate dipole moments. The units are debye units, named after the physical chemist Peter Debye (1884–1966).

Tip

Dipole moment is a measure of the overall polarity of a molecule. Mathematically it is the product of the magnitude of the charge multiplied by the distance between the charges. Where a molecule has several polar bonds, the overall dipole moment is the vector addition of the individual bond dipole moments taking into account both their size and direction.

Table 2.6 Measures of the polarities of some molecules.

Molecule	Dipole moment/ debye units
HCl	1.08
H_2O	1.94
CH_3Cl	1.86
$CHCl_3$	1.02
CCl_4	0
CO_2	0

A thin stream of a polar liquid is attracted towards an object with an electrostatic charge (Figure 2.35). This is because the polar molecules tend to move and rotate because the charge on one side of the molecules is attracted to the opposite charge on the object.

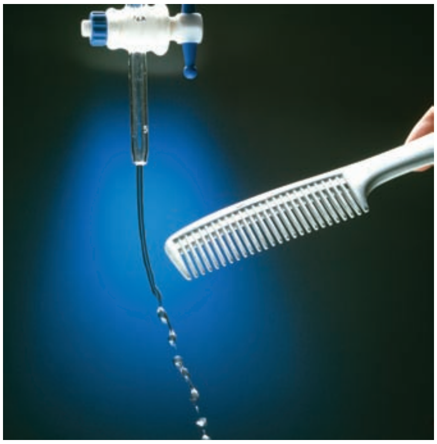


Figure 2.35 A thin stream of water is bent by a nearby comb carrying an electrostatic charge.

Test yourself

30 Consider the shapes of the following molecules and the polarity of their bonds. Then, divide the molecules into two groups – polar and non-polar: HBr, $CHBr_3$, CBr_4, CO_2, SO_2.

31 Account for the relative values of the dipole moments of the molecules in Table 2.6.

32 Draw the structure of the molecule OF_2 and use the symbols δ+ and δ– to show the polarity of the atoms in the bonds.

Compare your answer with the water molecule in Figure 2.32.

2.6 Intermolecular forces

The covalent bonds linking the atoms in the molecules (intramolecular forces) are relatively strong, whereas the forces between molecules (intermolecular forces) are weak. However, without these intermolecular forces there would be no rivers or oceans and the DNA double helix would not exist. Figure 2.36 shows another example of the effect of intermolecular forces.

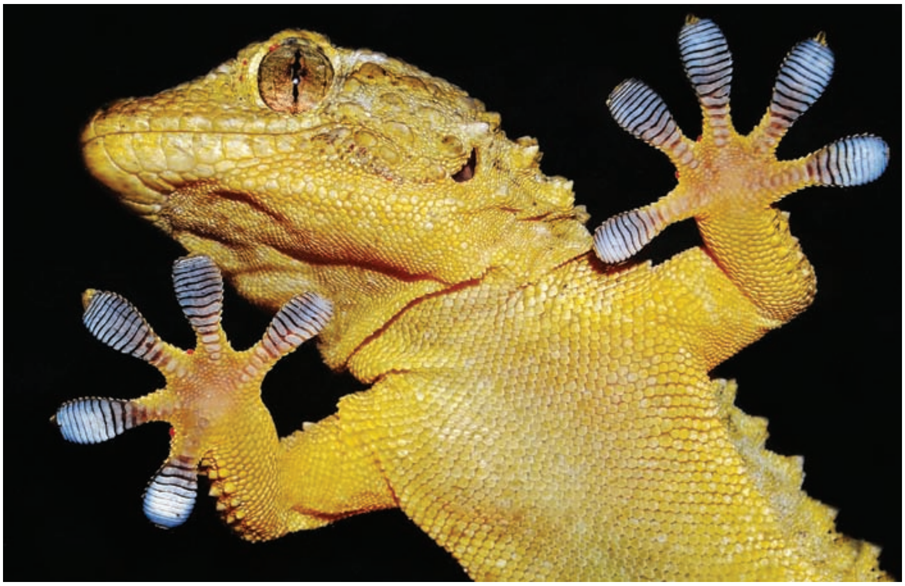


Figure 2.36 Geckos can climb smooth walls and hang from ceilings thanks to the intricate design of their feet. Each of a gecko's toes is lined with microscopic hairs, and each hair is further branched into finer structures. Weak intermolecular forces over the large surface area of the hairs are strong enough to grip on any surface, but weak enough to break as the gecko moves by peeling its feet away.

Key term

Intermolecular forces are weak attractive forces between molecules.

Intermolecular forces, as their name states, are forces *between* molecules. It is these forces which are overcome when a molecular substance melts or boils. The covalent bonds *within* a molecule are not broken when a substance melts or boils.

Tip

If you are ever confused about whether bonds or intermolecular forces are breaking, think what happens when water boils in a kettle. Vaporised water molecules come out of the spout because the forces between the water molecules are broken. However, hydrogen and oxygen gases are not formed! Boiling does not break the covalent bonds between oxygen and hydrogen atoms inside the water molecules.

Key term

London forces are the intermolecular forces that exist between all molecules. They arise from the attractions between temporary instantaneous dipoles and the fleeting dipoles they induce in neighbouring molecules.

London forces

The Dutch physicist Johannes van der Waals (1837–1923) developed a theory of intermolecular forces to explain why real gases behave in the way that they do. If there were no attractions between molecules, it would be impossible to turn a gas into a liquid by cooling. For some gases, the attractive forces are so weak that they do not liquefy until very low temperatures are reached. The boiling temperature of hydrogen, for example, is −253 °C, just 20 degrees above absolute zero.

It is not obvious why there are weak attractions between uncharged non-polar molecules, such as those of iodine, hydrocarbons and the noble gases. The German physicist who developed the theory to explain these forces was Fritz London (1900–1954), so they are sometimes called **London forces**.

When non-polar atoms or molecules meet, there are fleeting repulsions and attractions between the nuclei of the atoms and the surrounding clouds of electrons. Temporary displacements of the electrons lead to temporary dipoles as shown in Figure 2.37. These temporary instantaneous dipoles can induce dipoles in neighbouring molecules – positive poles induce negative poles and vice versa. The attractions between these instantaneous and induced dipoles are the weakest kind of intermolecular force, but their presence gives molecules a tendency to cohere. Intermolecular forces of this kind between small molecules are roughly a hundred times weaker than the covalent bonds within the molecules.

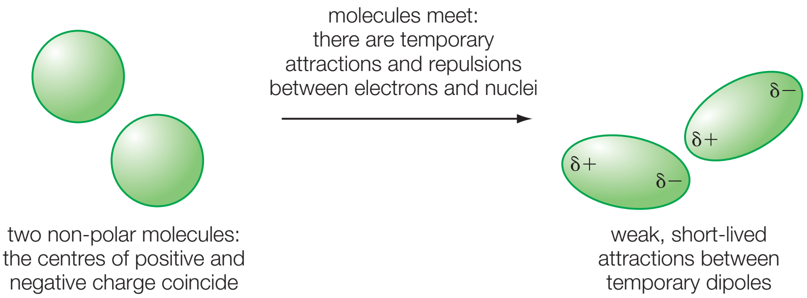


Figure 2.37 The origins of temporary induced dipoles.

Bigger molecules with a larger number of electrons have a higher **polarisability** and the possibility for temporary, induced dipoles is greater. This explains why the boiling temperatures of the elements rise down Group 7 (the halogens) and Group 0 (the noble gases) (see Figure 2.38). For the same reason, the boiling temperatures of alkanes increase with the increasing number of carbon atoms. The chemistry of the alkanes is considered in Sections 6.2.2 and 6.2.3.

Key term

Polarisability is an indication of the extent to which the electron cloud in a molecule (or an ion) can be distorted by a nearby electric charge.

The shapes of molecules can also affect the overall size of London forces. The attractions between long thin molecules are stronger than those between short fat molecules. This is because the attractions between long thin molecules can take effect over a larger surface area.

For a given volume, the minimum surface area is a sphere. Consider molecules with similar total volume but different surface areas, such as isomers of alkanes; the more branched the alkane, the more spherical and compact the molecule. This means that branched alkanes have a lower surface area of contact and therefore weaker London forces than unbranched isomers (see Activity: Intermolecular forces and the properties of alkanes).

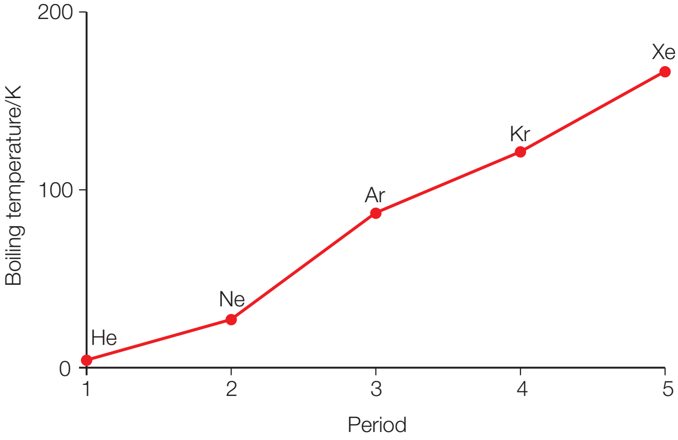


Figure 2.38 The boiling temperatures of noble gases plotted against atomic number.

Test yourself

33 Explain how Figure 2.38 illustrates the fact that the strength of intermolecular forces varies with the number of electrons in the molecules of monatomic gases.

34 **a)** Account for the states of the halogens at room temperature – chlorine is a gas; bromine is a liquid; while iodine is a solid.

b) Predict the state of the element astatine at room temperature and explain your answer.

Activity

Intermolecular forces and the properties of alkanes

Table 2.7 shows the melting and boiling temperatures of the lowest molecular mass alkanes. Use these data when answering the questions in this activity. Explain the patterns you find in terms of intermolecular forces.

Table 2.7 Melting and boiling temperatures of the lowest molecular mass alkanes.

Straight-chain alkanes		T_m/K	T_b/K
Methane	CH_4	91.1	109.1
Ethane	CH_3CH_3	89.8	184.5
Propane	$CH_3CH_2CH_3$	83.4	231.0
Butane	$CH_3(CH_2)_2CH_3$	134.7	272.6
Pentane	$CH_3(CH_2)_3CH_3$	143.1	309.2
Hexane	$CH_3(CH_2)_4CH_3$	178.1	342.1
Heptane	$CH_3(CH_2)_5CH_3$	182.5	371.5
Octane	$CH_3(CH_2)_6CH_3$	216.3	398.8
Nonane	$CH_3(CH_2)_7CH_3$	222.1	423.9
Decane	$CH_3(CH_2)_8CH_3$	243.4	447.2
Branched alkanes		**T_m/K**	**T_b/K**
2-Methylpropane	$(CH_3)_2CHCH_3$	113.7	261.4
2-Methylbutane	$(CH_3)_2CHCH_2CH_3$	113.2	301.0
2-Methylpentane	$(CH_3)_2CH(CH_2)_2CH_3$	119.4	333.4
2-Methylhexane	$(CH_3)_2CH(CH_2)_3CH_3$	154.8	363.1
2-Methylheptane	$(CH_3)_2CH(CH_2)_4CH_3$	164.1	390.7
2,2-Dimethylpropane	$C(CH_3)_4$	256.6	282.6

Boiling temperatures of the unbranched alkanes

Plot the boiling temperatures of unbranched alkanes against the number of carbon atoms in the molecules for the range C_1 to C_{10}.

1 Which of these alkanes are gases at room temperature and pressure and which are liquids?

2 What is the approximate increase in boiling temperature for each $-CH_2-$ added to an alkane chain?

3 Estimate the boiling temperature for dodecane, $C_{12}H_{26}$.

4 What type of intermolecular forces act between alkane molecules?

5 What two features of alkane molecules account for the trend in values shown by your graph?

Boiling temperatures of branched alkanes

Add to your graph the points for three 2-methyl alkanes, and also one for a 2,2-dimethyl alkane.

6 What is the effect of chain branching on the boiling temperatures of alkanes?

7 How do you account for this trend?

Melting temperatures of the unbranched alkanes

On the same axes as your other graphs, plot the melting temperatures of unbranched alkanes.

8 Identify one similarity and one difference between the plots of melting temperatures and boiling temperatures.

9 Suggest an explanation for the pattern of melting temperatures for alkanes with an odd number of carbon atoms compared to the alkanes with an even number of carbon atoms.

10 Polythene can be regarded as a long chain polymer of $-(CH_2)_n-$. The value of n can be around 100 000. How do you account for the strength of this material, which softens and melts in the range 100–150 °C?

Dipole–dipole interactions

Molecules with permanent dipoles attract each other a little more strongly than non-polar molecules. The positive pole of one molecule tends to attract the negative poles of others and vice versa (Figure 2.39).

This contribution to intermolecular forces from permanent dipoles occurs in addition to the London forces which act between all molecules.

Data such as boiling temperatures can be used to deduce the relative contribution of each type of force to the overall intermolecular forces.

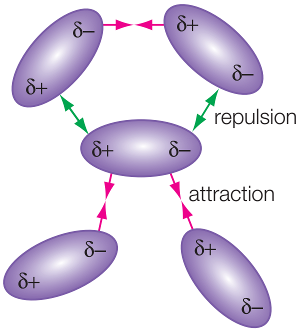


Figure 2.39 Forces between molecules with permanent dipoles.

Test yourself

35 Account for the difference in boiling temperature between the following pairs of molecules by considering both London forces and dipole–dipole attractions:

a) ethane which boils at −88 °C and fluoromethane which boils at −78 °C

b) butane which boils at −0.5 °C and propanone, CH_3COCH_3, which boils at 56 °C.

36 Iodine monochloride boils at 371 K and bromine boils at 332 K although both molecules contain exactly the same number of electrons. Explain why the boiling temperatures differ.

37 Three isomers with molecular formula C_7H_{16} (heptane, 3-methylhexane and 2,2-dimethylpentane) have boiling temperatures of 79.2 °C, 92.0 °C, and 98.4 °C, but not in that order.

a) Draw the structures of the three isomers.

b) Match the structures with their boiling temperatures and give your reasons.

Tip

Despite its name, a hydrogen 'bond' is an intermolecular force and not a covalent bond. Hydrogen bonds are at least 10 times weaker than covalent bonds. They affect the physical properties of many substances, but not the way they react.

Hydrogen bonding

Hydrogen bonding is an extreme type of dipole–dipole attraction between molecules. It is much stronger than other types of intermolecular force, but still at least 10 times weaker than covalent bonds. This strongest type of intermolecular force acts in addition to London forces.

Hydrogen bonding affects molecules in which hydrogen is covalently bonded to one of the three highly electronegative elements – fluorine, oxygen and nitrogen.

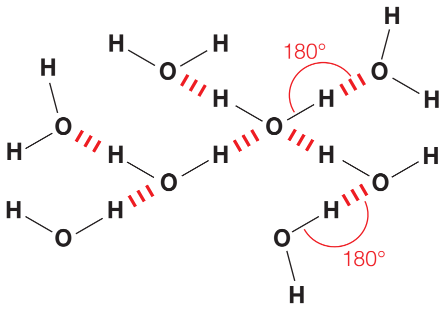


Figure 2.40 Hydrogen bonding in water.

The highly electronegative atom attracts electrons strongly away from hydrogen so the covalent bond between them is extremely polar and the hydrogen atom is very electron deficient or δ+. A strong intermolecular force then results between this δ+ hydrogen atom and a lone pair of electrons on the δ− fluorine, oxygen or nitrogen atom of a nearby molecule.

The three atoms associated with a hydrogen bond are always in a straight line. According to electron-pair repulsion theory, the bonding pair of electrons in the covalent bond to hydrogen and the lone pair of electrons on the fluorine, oxygen or nitrogen atom of the adjacent molecule keep as far apart as possible to minimise the repulsion between them. So the angle between the covalent bond to hydrogen and the hydrogen bond is 180° (see Figures 2.40 and 2.41).

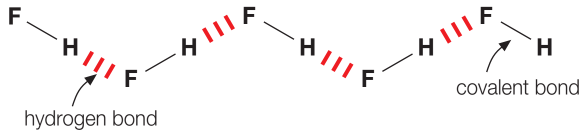


Figure 2.41 Hydrogen bonding in hydrogen fluoride.

Key term

Hydrogen bonding

A strong intermolecular force between a δ+ hydrogen atom covalently bonded to fluorine, oxygen or nitrogen and a lone pair of electrons on the δ− fluorine, oxygen or nitrogen atom of a nearby molecule.

The essential requirements for **hydrogen bonding** are:

- a hydrogen atom covalently bonded to a highly electronegative atom
- a lone pair of electrons on a second electronegative atom.

In a water molecule there are two O−H bonds and two lone pairs on the oxygen atom. This means that each water molecule can take part in up to four hydrogen bonds, two via the hydrogen atoms and two others via the lone pairs of electrons (see Figure 2.42). This helps to explain the three-dimensional structure of ice (Figure 2.43). In liquid water, molecular motion means that not all possible hydrogen bonds are formed at all times.

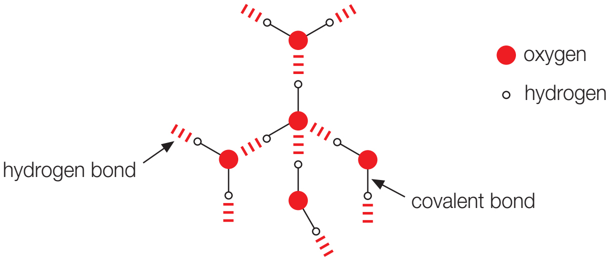


Figure 2.42 Molecules in ice are held together by hydrogen bonding. Each oxygen atom is bonded to two hydrogen atoms by covalent bonds and two others by hydrogen bonds.

Hydrogen bonding accounts for:

- the relatively high boiling temperatures of ammonia, water and hydrogen fluoride, which are out of line with those of the other hydrides in Groups 4, 5 and 6 (see Figure 2.44)
- the open structure (see Figure 2.43) and low density of ice (see Figure 2.45)
- the solubility of simple alcohols in water
- the pairing of bases in a DNA double helix.

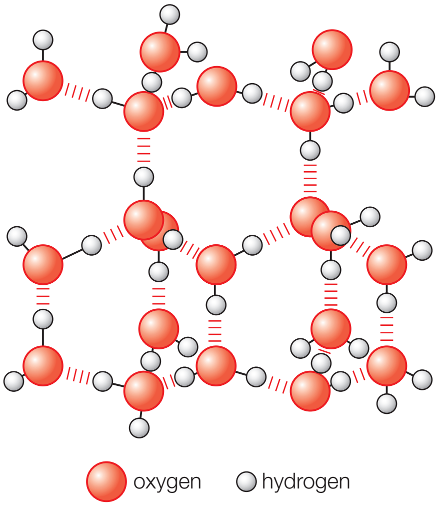


Figure 2.43 The hydrogen bonding in ice holds the water molecules in an open structure. This structure collapses as the ice melts. The molecules then get closer together so the density rises to a maximum at 4 °C.

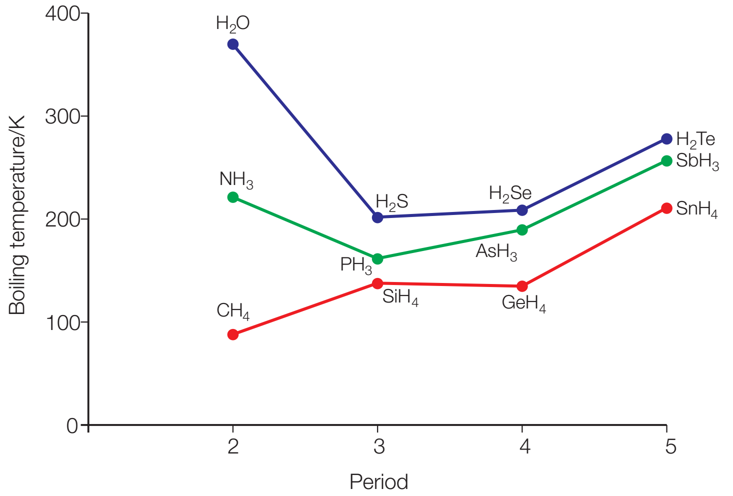


Figure 2.44 Boiling temperatures for the hydrides of the elements in Groups 4, 5 and 6.

Test yourself

38 Draw diagrams to show hydrogen bonding between water molecules and:

a) ammonia molecules in a solution of ammonia, NH_3

b) ethanol molecules in a solution of ethanol, CH_3CH_2OH.

39 a) The boiling temperatures of the hydrogen halides are shown in Table 2.8. Plot a graph showing how the boiling temperatures of the hydrogen halides vary with the atomic number of the halogen.

b) Describe and explain the pattern shown by the graph with reference to the types of intermolecular forces which act between the molecules.

Table 2.8 Boiling temperatures of the hydrogen halides.

Hydrogen halide	T_b/K
Hydrogen fluoride	293
Hydrogen chloride	188
Hydrogen bromide	206
Hydrogen iodide	238

40 Explain the differences in Figure 2.44 between the plot for the hydrides of Group 6 and the plot for the hydrides of Group 4.

41 Which types of intermolecular force hold the molecules together in:

a) hydrogen bromide, HBr

b) propane, $CH_3CH_2CH_3$

c) methanol, CH_3OH?

Figure 2.45 An iceberg in Antarctica. Only about 10% of the ice is above the surface of the sea because ice is less dense than water at 0 °C.

2.7 Solutions and solubility

Patterns of solubility

As a rough-and-ready rule, 'like dissolves like'. Water, which is highly polar, dissolves many ionic compounds and compounds with −OH groups such as alcohols and sugars. Non-polar solvents, such as cyclohexane, dissolve hydrocarbons, molecular elements and molecular compounds.

But there is a limit to the quantity of a substance, a **solute**, that can dissolve in a **solvent**. A **saturated solution** is one which contains as much of the dissolved solute as possible at a particular temperature. The **solubility** is at maximum in a saturated solution.

Key terms

A **solute** is a chemical which dissolves in a **solvent** to make a solution.

A **saturated solution** contains as much of the solute as possible at a particular temperature.

Solubility is a measure of the concentration of a saturated solution of a solute at a specified temperature. Solubilities are commonly recorded as 'mol per 100 g water' or 'g per 100 g water' at 25 °C (298 K).

Soluble or insoluble?

No chemicals are completely soluble and none are completely insoluble in water. Even so, chemists find it useful to use a rough classification of solubility based on what they see on shaking a little of the solid with water in a test tube:

- very soluble, like potassium nitrate – plenty of the solid dissolves quickly
- soluble, like copper(II) sulfate – crystals visibly dissolve to a significant extent
- sparingly or slightly soluble, like calcium hydroxide – little solid seems to dissolve but, in this case, the pH of the solution changes
- insoluble, like iron(III) oxide – no sign that any of the material dissolves.

A similar rough classification applies to gases dissolving in water. Ammonia and hydrogen chloride are very soluble; sulfur dioxide is soluble; carbon dioxide is slightly soluble; helium is insoluble.

Tip

The term 'saturated' is also used in organic chemistry to describe compounds which contain only single bonds. In hydrogenation reactions, hydrogen adds across double or triple bonds in unsaturated hydrocarbons. The saturated compounds formed contain as much hydrogen as possible.

Solubility and intermolecular forces

Patterns of solubility for molecular solids are determined by intermolecular forces. The dissolving of a molecular solute is shown in Figure 2.46. Three interactions are involved:

- the intermolecular forces between solute molecules
- the intermolecular forces between solvent molecules
- the intermolecular forces between solute and solvent molecules.

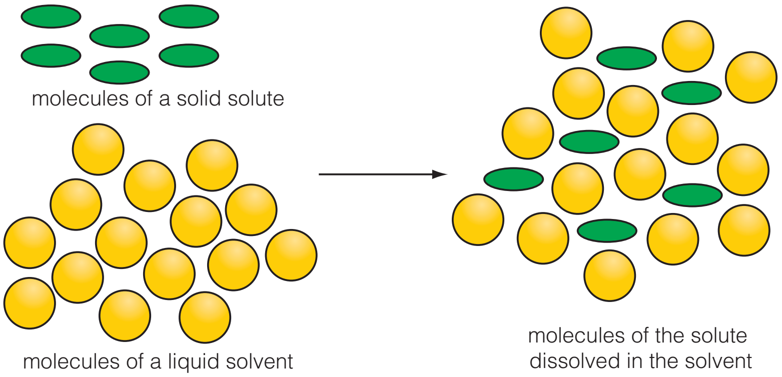

molecules of a solid solute
molecules of a liquid solvent
molecules of the solute dissolved in the solvent

Figure 2.46 A molecular substance dissolves if the energy needed to break intermolecular forces and to separate the molecules in the solute and in the solvent is about the same as the energy released as the solute forms new intermolecular forces with the solvent.

When all three types of force are about the same strength, the solute dissolves freely in the solvent. So non-polar molecules, such as those of a hydrocarbon wax, dissolve and mix freely with non-polar liquids such as cyclohexane. In this example, cyclohexane is acting as a **non-aqueous solvent**. All the intermolecular forces involved are London forces.

Key term

A **non-aqueous solvent** is any solvent other than water.

However, non-polar molecules, such as hydrocarbons, do not dissolve in water. The non-polar molecules can separate easily because their intermolecular forces are relatively weak. But the stronger hydrogen bonding between water molecules acts as a barrier which keeps out molecules that cannot, themselves, form hydrogen bonds.

Polar organic molecules, such as halogenoalkanes, are also insoluble in water. Again the weak dipole-dipole forces between the organic molecules allow them to separate fairly easily. But, as they cannot form hydrogen bonds with water, they cannot disturb the hydrogen bonding between the water molecules and so remain separate from water.

Organic molecules that can form hydrogen bonds, such as alcohols, do dissolve and mix with water. Ethanol molecules, for example, can break into the hydrogen-bonded structure of water by forming new hydrogen bonds between ethanol and water molecules.

The two liquids, ethanol (C_2H_5OH) and water, are **miscible**. Alcohols with longer hydrocarbon chains do not mix with water so easily. The longer the chain, the less the miscibility of the alcohol with water.

Key term

Miscible liquids are those which mix with each other – water and ethanol are miscible; oil and water are immiscible.

Solutions of ionic salts in water

It is not obvious why the charged ions in a crystal of sodium chloride can separate and dissolve in water with only a small energy change. The high melting point of a salt such as sodium chloride (801 °C) shows that a large amount of energy is needed to separate the ions from a crystal.

The explanation of the solubility of some ionic salts in water is that the ions are strongly hydrated by polar water molecules (Figure 2.47). The water molecules cluster around the ions and bind to them. The energy released when the water molecules bind to the ions is enough to compensate for the energy needed to overcome the electrostatic attractions holding the ionic lattice together.

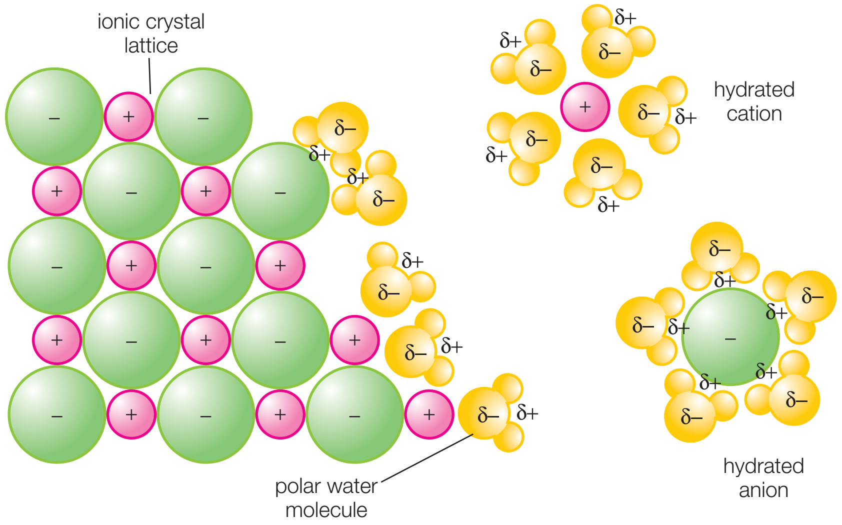


Figure 2.47 Sodium ions and chloride ions leaving a crystal lattice and becoming hydrated as they dissolve in water. Here the bonding between the ions and the polar water molecules is electrostatic attraction.

Other salts are insoluble in water because the **hydration** energy that would be released when the ions are hydrated is not large enough to overcome the electrostatic forces in the lattice of the crystals.

Key term

Hydration takes places when water molecules bond to ions or add to molecules. Water molecules are polar so they are attracted to both positive ions and negative ions.

Tip

Not all reactions which occur are exothermic; some reactions do occur despite being endothermic. Similarly, some substances dissolve in water even though the overall enthalpy change of solution is endothermic. The reason for this is that other factors are involved when a solution forms, including the disorder created as the solute particles move apart into the solvent. The overall energy change which takes these other factors into account is called the Gibbs free energy change and will be considered in detail later.

Test yourself

42 Explain why methane gas is insoluble in water, but ammonia is freely soluble.

43 Explain why iodine is soluble in a non-aqueous solvent such as cyclohexane, but almost insoluble in water.

44 Explain why methanol is miscible with water whereas decan-1-ol is not.

45 Table 2.9 shows the solubility in water of several salts.

Table 2.9 Solubility in water of some Group 1 and Group 2 salts.

Salt	Solubility in mol/100 g water
Barium sulfate	9.43×10^{-7}
Caesium fluoride	3.84
Calcium hydroxide	1.53×10^{-3}
Calcium sulfate	4.66×10^{-3}
Lithium chloride	2.00
Lithium fluoride	5.09×10^{-3}
Magnesium chloride	5.57×10^{-1}
Magnesium sulfate	1.83×10^{-1}
Potassium iodide	8.92×10^{-1}

Use the data in Table 2.9 to classify the salts as very soluble, soluble, slightly soluble or insoluble according to their solubility in water.

2.8 Giant covalent structures

A few non-metal elements – including carbon and silicon – consist of giant structures of atoms held together by covalent bonding.

Some compounds of non-metals, such as silicon dioxide and boron nitride, also exist as giant covalent structures. The covalent bonds in these structures are strong, so giant covalent substances are very hard and have very high melting temperatures.

Test yourself

46 Carbon dioxide is a gas at room temperature, whereas silicon dioxide (silicon(IV) oxide) is a solid with a very high melting point.

Explain this difference in terms of the structures of the two compounds.

47 Consider the structure of silicon dioxide (Figure 2.48) which shows that each silicon atom is bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms. Confirm that, overall, there are two oxygen atoms for every one silicon atom and, therefore, the (empirical) formula of silicon dioxide is SiO_2. Drawing a planar representation of Figure 2.48 may help.

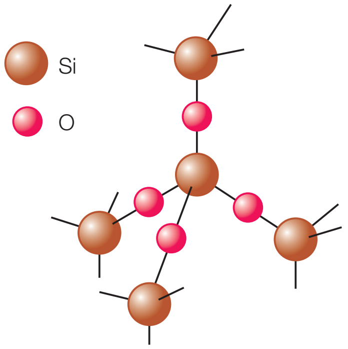


Figure 2.48 Part of the giant structure of silicon dioxide in the mineral quartz. Silicon atoms are arranged in the same way as carbon atoms in diamond, but with an oxygen atom between each pair of silicon atoms. Sandstone and sand consist mainly of silicon dioxide.

Structure and bonding in different forms of carbon

Carbon can exist in different solid forms – diamond, graphite, various fullerenes and graphene. These solid forms of carbon are called **allotropes** – different forms of the same element in the same physical state.

These forms of carbon illustrate the important connections between the structure and bonding of materials, their properties and hence their uses.

All these forms of carbon are held together by strong covalent bonds with a definite length and direction. Diamond, graphite and graphene are giant covalent structures, whereas fullerenes, in comparison, are relatively simple molecules.

Key term

Allotropes are different forms of the same element in the same physical state.

Diamond

Strong covalent bonds with a definite length and fixed direction help to account for the rigid covalent structure of diamond (Figure 2.49). It is the hardest naturally occurring substance with a high sublimation point. People have always valued diamonds for their brilliance as gemstones. But diamonds are also used industrially as abrasives for cutting and grinding hard materials such as glass and stone (Figure 2.50).

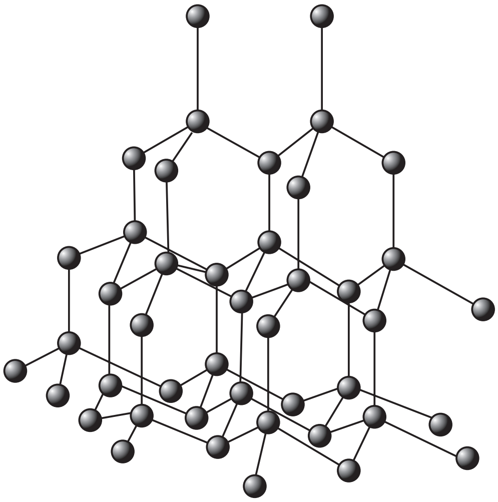


Figure 2.49 Part of the giant covalent structure in diamond – each carbon atom is linked to four other atoms in a network extending throughout the giant structure.

Figure 2.50 Diamonds that cannot be sold as gemstones are used in glass cutters and diamond-studded saws. This photo shows an engraver using a diamond-studded wheel to make patterns on a glass.

Diamond does not conduct electricity because the electrons in its covalent bonds are fixed (localised) between pairs of atoms.

Diamond conducts thermal energy very well – five times better than copper. This important property means that diamond-tipped cutting tools don't overheat. The rigidity of the strong covalent bonds in diamond means that, as the atoms close to the tip of a cutting tool get hotter and move faster, the vibrations move rapidly throughout the giant structure.

Graphite

Graphite is used to make crucibles for molten metals. It can withstand high temperatures because it sublimes at the extremely high temperature of 3650 °C. For the same reason, graphite blocks are used to line the walls of industrial furnaces.

This high sublimation temperature also suggests that graphite has a giant structure with strong covalent bonds. This is confirmed by X-ray diffraction studies which show that the atoms are held together in extended sheets (layers) of atoms. Each layer contains billions and billions of carbon atoms arranged in hexagons (Figure 2.51). Each carbon atom is held strongly in its layer by strong covalent bonds to three other carbon atoms. So every layer is a giant covalent structure. The distance between neighbouring carbon atoms in the same layer is only 0.14 nm, but the distance between layers is 0.34 nm.

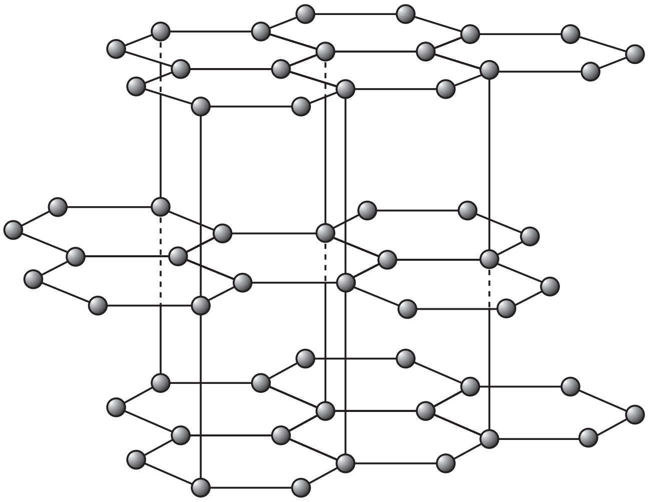


Figure 2.51 The giant covalent structure of graphite. The layers are vast sheets of carbon atoms piled on top of each other. The bonding between atoms within the layers is strong, but the bonding between layers is relatively weak.

Each carbon atom in graphite uses three of its outer shell electrons to form three normal covalent bonds with other carbon atoms. This accounts for the trigonal arrangement of bonds around each atom and the hexagonal arrangement of the atoms within a layer.

The fourth outer shell electron on each carbon atom forms part of a cloud of delocalised electrons spread out over each layer. Because of these delocalised electrons, graphite conducts electricity well. This explains why graphite is used for electrodes in industry and as the positive terminal in cells.

The covalent bonds between carbon atoms within the layers of graphite are so strong that many modern **composites** incorporate graphite fibres for greater tensile strength (Figure 2.52).

Key term

Composites combine two or more materials to create a new material which has the desirable properties of both its constituents. For example, plastic reinforced with graphite fibres combines the flexibility of the plastic with the high tensile strength of graphite.

Unlike diamond, graphite is soft and feels greasy – this property leads to the use of graphite as a lubricant. It has lubricating properties because the bonding between the well-separated layers is relatively weak, allowing the layers to slide over each other.

Figure 2.52 Graphite fibres are used to reinforce the shafts of broken bones, badminton rackets and golf clubs, like the one being used by Rory McIlroy in this photo.

Fullerenes

At one time, chemists believed there were only two forms of crystalline carbon. Then, in 1985, Harry Kroto and his research team at the University of Sussex, working with teams led by Bob Curl and Richard Smalley in Texas, discovered buckminsterfullerene, C_{60} – a black solid with a simple molecular structure. Since 1985, several similar subtances have been prepared; these are now known as 'fullerenes'.

At the molecular level, the fullerenes mimic the geodesic (football-like) dome invented by the American engineer Robert Buckminster Fuller (Figure 2.53). Hence, the original name 'buckminsterfullerene' and the nicknames 'bucky balls' and 'footballene'.

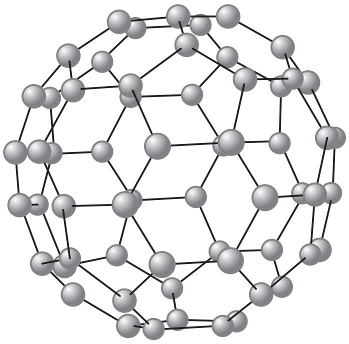


Figure 2.53 The structure of C_{60} is roughly spherical with each carbon atom bonded to three nearest neighbours. Look carefully and see if you can count all 60 carbon atoms. Other fullerenes have the formulae C_{32}, C_{50} and C_{240}.

Fullerenes are fundamentally different from diamond and graphite because they are molecular forms of carbon, rather than infinite giant covalent structures.

Fullerenes are black solids which are soluble in various solvents because of their molecular structure. This has already led to the use of C_{60} in mascara and printing ink.

The bonding at each carbon atom in fullerenes resembles that in graphite. Three of the outer shell electrons are combined in covalent bonds with other atoms, while the fourth electron is delocalised over the whole molecule. But, unlike graphite which conducts, the fullerenes are good electrical insulators because the delocalised electrons cannot move between molecules. However, metals in Groups 1 and 2 can react with C_{60} to form superconducting systems at very low temperatures. The reaction produces a rare type of salt in which electrons transferred to the C_{60} move around the whole salt in the same way as electrons move in a metal.

$$3Rb(s) + C_{60}(s) \rightarrow (Rb^+)_3C_{60}{}^{3-}(s)$$

At present, these superconducting fullerene–metal systems can conduct only relatively small currents at very low temperatures, below −190 °C. The priority is to develop superconductors that can work at higher temperatures and carry much larger currents.

Now that chemists understand the structure of fullerenes, they are able to produce fullerenes in the form of tubes as well as spheres. These 'buckytubes' or 'carbon nanotubes' are not only the narrowest tubes ever made, but also the strongest and toughest weight for weight.

These carbon nanotubes have enormous potential in very diverse applications, from the replacement of graphite fibres in golf clubs and fishing rods to their use in medicine as vehicles for carrying drugs into specific body cells.

Graphene

Graphene is effectively a two-dimensional material although essentially a one–atom thick layer of carbon atoms, the same as a single layer of graphite. Graphene, first isolated in 2003 in Manchester by Andre Geim (Figure 2.54) and Kostya Novoselov, is an exciting new materials with a huge number of possible uses.

It is the thinnest material known but is also one of the strongest. Graphene-plastic composites are extremely strong but very light weight and so have potential uses in aircraft and cars.

Graphene is as good a conductor of electricity as copper and is also a better conductor of heat than any other material. Composites again allow the possibility of plastics which conduct.

Graphene's transparency, flexibility (see Figure 2.55) and conductivity also raise the possibility of its use in touchscreens for mobile devices. It is also being investigated for use in ultrasensitive chemical sensors and photocells.

Figure 2.54 Professor Andre Geim holding a model of graphene. Working with Kostya Novoselov at the University of Manchester, he isolated this single layer structure in 2003. They were jointly awarded the Nobel Prize for Physics in 2010 for their work.

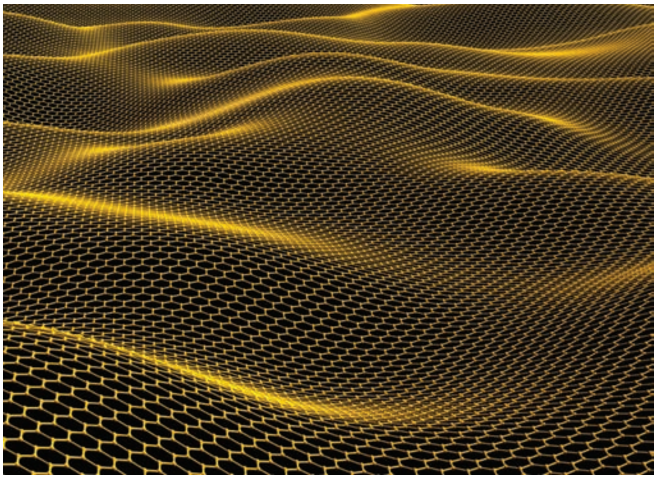


Figure 2.55 Computer model of the molecular structure of graphene.

Test yourself

48 **a)** Why does a zip fastener move more freely if it is rubbed with a soft pencil?

b) Why should you use a pencil for this rather than oil?

c) Why is graphite sometimes mixed with the oil used to lubricate the moving parts of machinery?

49 **a)** Name one element, other than carbon, which exists as different allotropes and name the allotropes.

b) Explain what is meant by a 'composite'. Illustrate your answer with an example, such as reinforced concrete or fibre glass (glass-reinforced plastic).

50 **a)** Why is diamond such a poor conductor of electrical energy, but a good conductor of thermal energy?

b) Why does graphene conduct electricity but fullerenes do not?

2.9 Metallic bonding and structures

Metals are very important and useful materials. Just look around you and notice the uses of different metals – in vehicles, bridges, pipes, taps, radiators, cutlery, pans, jewellery and ornaments. X-ray studies show that the atoms in most metals are packed together as closely as possible. This arrangement is called 'close packing'.

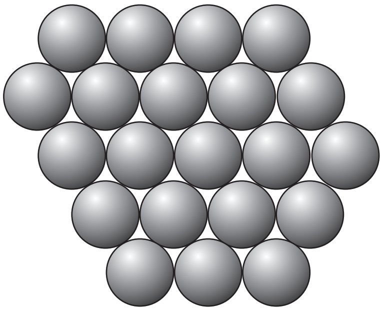


Figure 2.56 Close packing of atoms in one layer of a metal.

Figure 2.56 shows a model of a few atoms in one layer of a metal crystal. Notice that each atom in the middle of the layer 'touches' six other atoms in the same layer.

When a second layer is placed on top of the first, atoms in the second layer sink into the dips between atoms in the first layer (Figure 2.57).

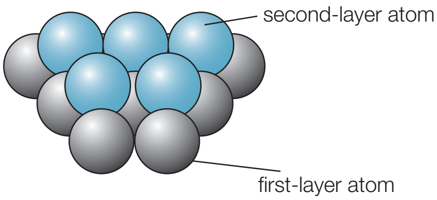


Figure 2.57 Atoms in two layers of a metal crystal.

This packing arrangement allows atoms in one layer to get as close as possible to those in the next layer, so the structure of most metals is a giant lattice of closely packed atoms in a regular pattern. In this giant lattice, electrons in the outer shell of each metal atom are free to drift through the whole structure. These electrons do not have fixed positions – they are described as '**delocalised electrons**'.

So, **metallic bonding** consists of positive ions with electrons moving around and between them as a 'sea' of delocalised negative charge (Figure 2.58).

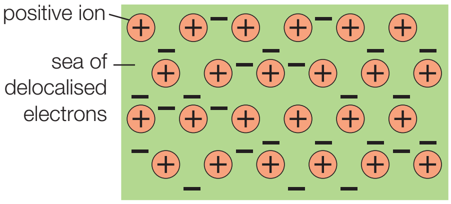


Figure 2.58 Metallic bonding results from the strong attractions between metal ions and the sea of delocalised electrons.

The strong electrostatic attractions between the positive metal ions and the 'sea' of delocalised electrons result in strong forces between the metal atoms.

The properties of metals

In general, metals:

- have high melting and boiling temperatures
- have high densities
- are good conductors of heat and electricity
- are malleable – can be bent or hammered into different shapes.

Key terms

Delocalised electrons are bonding electrons which are not fixed in a bond between two atoms. They are free to move and are shared by many atoms.

Metallic bonding is the strong electrostatic attraction between metal ions and the 'sea' of delocalised electrons.

Tip

Metals in Group 1 have lower melting temperatures than other metals, for example, sodium melts at 98 °C. An irregular piece of sodium melts to form a sphere as it reacts on the surface of cold water. Atoms of Group 1 metals have only one electron in their outer energy level, so the delocalised cloud contains only one electron per atom and the metallic bonding is relatively weak. Magnesium (two outer electrons) and aluminium (three outer electrons) and the transition metals have more delocalised electrons per atom, so the forces of attraction in the lattice and the resulting melting temperatures are higher than for sodium.

Tip

It is often convenient to reduce the malleability of a metal to make it harder. This can be achieved by adding other metals or carbon to the metal. Atoms of different sizes in the lattice disrupt the layers of atoms and make it more difficult for layers to slide over each other. These mixtures are called alloys and have important engineering uses, e.g. the addition of a few percent of tungsten and molybdenum to iron produces harder steel used for high speed drill bits.

All the properties of metals can be explained and interpreted in terms of their close-packed structure and delocalised electrons.

- *High melting and boiling temperatures* – metal atoms are closely packed with strong forces of attraction between the positive ions and delocalised electrons. So, it takes a lot of energy to move the positive ions away from their positions in the giant lattice, allowing the metal to melt. It takes even more energy to separate individual atoms in the metal at the boiling temperature.
- *High densities* – the atoms are close packed with as little space between them as possible.
- *Good conductors of heat* – when a metal is heated, energy is transferred to the electrons. The delocalised electrons in the heated region move around faster and conduct the heat (energy) rapidly to other parts of the metal.
- *Good conductors of electricity* – when a potential difference is applied across a metal, the delocalised electrons are attracted to the positive electrode and flow through the metal. This flow of electrons is an electric current.
- *Malleable* – the bonds between metal atoms are strong, but they are not directional because the delocalised electrons can drift throughout the lattice and attract any of the positive ions. When a force is applied to a metal, lines or layers of atoms can slide over each other. This is known as 'slip'. After slipping, the atoms settle into close-packed positions again. Figure 2.59 shows the positions of atoms before and after slip. This is what happens when a metal is bent or hammered into different shapes.

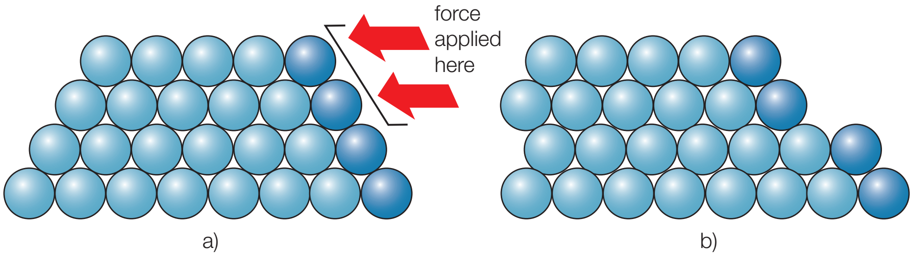


Figure 2.59 Positions of atoms in a metal a) before and b) after 'slip' has occurred.

Test yourself

51 Why are the electrons in the outermost shell of metal atoms described as 'delocalised'?

52 Look carefully at Figures 2.56 and 2.57.

- **a)** Choose one central atom in a layer. How many atoms in the same layer touch this atom?
- **b)** How many atoms in the layer above this first layer also touch this atom?
- **c)** In total, how many atoms touch a single metal atom in a close-packed arrangement.

53 Explain why most metals:

- **a)** have high densities
- **b)** are good conductors of electricity.

54 Name a metal or alloy and its particular use to illustrate each of the following typical properties of metals:
- **a)** shiny
- **b)** conduct electricity
- **c)** bend without breaking
- **d)** high tensile strength.

55 Consider the patterns of metal properties in the periodic table.
- **a)** Which metals have:
  - **i)** relatively high densities
  - **ii)** relatively low densities?
- **b)** Which metals have:
  - **i)** relatively high melting temperatures
  - **ii)** relatively low melting temperatures?

Figure 2.60 Blacksmiths rely on the malleability of metals to hammer and bend them into useful shapes.

Activity

Choosing metals for different uses

Various properties of six metals are shown in Table 2.10.

Table 2.10 Some metals and their properties.

Metal	Density/$\mathrm{g\,cm^{-3}}$	Tensile strength/ $10^7\,\mathrm{N\,m^{-2}}$	Melting temperature/°C	Electrical resistivity/ $10^{-8}\,\mathrm{ohm\,m}$	Thermal conductivity/ $\mathrm{J\,s^{-1}\,cm^{-1}\,K^{-1}}$	Cost per tonne/£
Aluminium	2.7	8	660	2.5	2.4	960
Copper	8.9	33	1083	1.6	3.9	1200
Iron	7.9	21	1535	8.9	0.8	130
Silver	10.5	25	962	1.5	4.2	250000
Titanium	4.5	23	1660	43.0	0.2	27000
Zinc	7.1	14	420	5.5	1.1	750

1 Use the information in Table 2.10 to explain the following statements.
- **a)** Copper is used in most electrical wires and cables, but high-tension cables in the National Grid are made of aluminium.
- **b)** Bridges are built from steel which is mainly iron, even though the tensile strength of iron is lower than that of some other metals.
- **c)** Metal gates and dustbins are made from steel coated with zinc (galvanised).
- **d)** Silver is no longer used to make our coins.
- **e)** Aircraft are now constructed from an aluminium/titanium alloy, rather than pure aluminium.
- **f)** The base of high-quality saucepans is copper rather than steel (iron).

2 If the atoms in a metal pack closer together then the density should be higher, the bonds between atoms should be stronger and so the melting temperature should be higher. This suggests there should be a relationship between the density and melting temperature of a metal.

Use the data in the table to check if there is a relationship between density and melting temperature. State ‘yes’ or ‘no’ and explain your answer.

3 The explanation of both electrical and thermal conductivity in metals uses the concept of delocalised electrons. This suggests that there should be a relationship between the electrical and thermal conductivities of metals.

Use the data in the table to check if there is a relationship. (Hint: electrical resistivity is the reciprocal of electrical conductivity.) State ‘yes’ or ‘no’ and explain your answer.

Activity

Structure, bonding and physical properties

The physical properties of a substance can be predicted knowing its structure and bonding. Similarly, structure and bonding can be deduced from physical properties. In this activity you will predict the physical properties of a substance in terms of its structure and bonding and then use numerical data to predict the type of structure and bonding. Solids exist in four types of structure; these types and some properties are shown in Table 2.11.

Table 2.11 The four types of solid structure and some properties.

Type of structure	**Giant ionic lattice**	**Giant metallic lattice**	**Simple molecular (covalent)**	**Giant covalent lattice**
Type of substance	Compound of metal and non-metal	Metal element	Non-metal element or compound of non-metals	Non-metal element or compound of non-metals
Attraction between particles	Strong	Strong	Weak	Strong
Melting temperature		Mostly high		
Electrical conductivity of solid	Poor		Poor	Poor
Solubility in water				
Example				

1 Copy and complete the table by adding the missing properties and examples.

2 State why solid ionic compounds do not conduct electricity and explain under what conditions ionic compounds can be electrolysed.

3 Transition metals have high melting temperatures. Give an example of a group of metals with much lower melting temperatures and suggest why these are different from transition metals.

4 Explain why simple molecular solids are poor electrical conductors. Give an example of a simple molecular substance which conducts when dissolved in water and explain why the solution conducts electricity.

5 Name a giant covalent substance which does conduct electricity and explain why it is a conductor.

6 Table 2.12 gives some properties of substances A to H. Use this information to identify the type of bonding and structure of these substances. It is not expected that the actual identity of each substance is deduced.

Table 2.12 Some properties of the substances A–H.

	Melting temperature/K	**Boiling temperature/K**	**Electrical conductivity as solid**	**Electrical conductivity as liquid**	**Electrical conductivity in aqueous solution**
A	918	1563	Poor	Good	Good
B	162	319	Poor	Poor	Poor
C	2345	3253	Poor	Good	Insoluble
D	302	942	Good	Good	Good
E	185	206	Poor	Poor	Good
F	1883	2503	Poor	Poor	Insoluble
G	1728	3003	Good	Good	Insoluble
H	279	353	Poor	Poor	Insoluble

Exam practice questions

1 The table shows the melting temperatures of the elements in Period 3 of the periodic table.

Element	Melting temperature/K
Na	371
Mg	922
Al	933
Si	1683
P	317
S	386
Cl	172
Ar	84

a) Explain why the melting temperature of sodium is much lower than that of magnesium. *(3)*

b) Phosphorus and sulfur exist as molecules of P_4 and S_8, respectively. Explain their difference in melting temperatures. *(2)*

c) State the type of structure and the nature of the bonding in each of the following elements:

i) aluminium **ii)** silicon
iii) chlorine. *(6)*

2 This question is about calcium and calcium oxide.

a) i) Describe the bonding in calcium. *(3)*

ii) Explain why calcium is a good conductor of electricity. *(2)*

b) Draw dot-and-cross diagrams for the ions in calcium oxide showing *all* the electrons and the ionic charges. *(4)*

c) Under what conditions does calcium oxide conduct electricity? Explain your answer. *(6)*

3 a) Using sodium chloride, hydrogen chloride and copper, explain what is meant by covalent, ionic and metallic bonding. *(9)*

b) Compare and explain the conduction of electricity by sodium chloride and copper in terms of structure and bonding. *(3)*

c) By considering their lattice structures, explain why sodium chloride is brittle but copper is malleable. *(3)*

4 a) Draw dot-and-cross diagrams, with outer shell electrons only, to show the bonding in ammonia and water. *(2)*

b) On mixing with water, ammonia reacts to form an alkaline solution containing ammonium ions and hydroxide ions.

i) Write an equation for this reaction, including state symbols. *(2)*

ii) The ammonium ion has dative covalent bonding. Explain the term 'dative covalent bonding'. *(2)*

iii) Draw a dot-and-cross diagram of the ammonium ion and label the dative covalent bond. *(2)*

5 Draw dot-and-cross diagrams of the following molecules and ions. Predict the shape and give the bond angle in each case.

a) H_3O^+ *(4)*

b) IF_5 *(4)*

c) ClO_3^- *(4)*

d) PO_4^{3-} *(4)*

6 a) Phosphorus forms the chloride PCl_3. Draw a dot-and-cross diagram for PCl_3. *(2)*

b) Draw and name the shape of the PCl_3 molecule and give the bond angle. *(3)*

c) Explain why PCl_3 has this shape and this angle. *(3)*

d) Why does PCl_3 form a stable compound with BCl_3? *(3)*

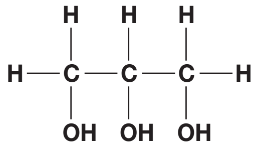
e) State the Cl−P−Cl bond angle and the Cl−B−Cl bond angle in the compound formed and explain your answer. *(3)*

7 a) State the types of intermolecular forces present in:

i) propane **ii)** ethanol. *(2)*

b) Why is the boiling temperature of propane (−42.2 °C) lower than the boiling temperature of ethanol (78.5 °C)? *(2)*

c) Glycerol (IUPAC name propane-1,2,3-triol) is a type of alcohol.



Explain why glycerol is very viscous and predict whether the boiling temperature of glycerol is higher or lower than that of ethanol, giving your reasons. *(3)*

8 Deduce the shapes of the molecules CF_4, SF_4 and XeF_4 and compare their overall polarity. *(6)*

9 Explain why:

a) FCl is polar but F_2 is not *(2)*

b) SO_2 is polar but CO_2 is not *(2)*

c) NCl_3 is polar but BCl_3 is not. *(2)*

10 a) Name the strongest of the intermolecular forces between water molecules, and describe the bonding with the help of a diagram. *(3)*

b) Explain why:

i) the boiling temperature of water is higher than the boiling temperatures of the other hydrides of Group 6 elements

ii) ice is less dense than water at 0 °C

iii) water and pentane are immiscible liquids

iv) methoxymethane ($CH_3{-}O{-}CH_3$) boils at −24.8 °C but ethanol, an isomer of methoxymethane, boils at 78.5 °C. *(8)*

11 Diamond and graphite are described as allotropes.

a) Explain what is meant by the term 'allotropes'. *(2)*

b) Are fullerenes and graphene also allotropes with diamond and graphite? Explain your answer. *(1)*

c) Graphite fibres are often used for the brushes (contacts) in electric motors.

i) Give two reasons why graphite fibres are used in this way. *(2)*

ii) Give three reasons why diamonds would be unsuitable for this use. *(3)*

12 The covalently bonded compound urea has the formula $(NH_2)_2C{=}O$. Urea is commonly used as a fertiliser in most of Europe, whereas ionic ammonium nitrate, NH_4NO_3, is the most popular fertiliser in the UK.

a) Draw a dot-and-cross diagram for urea. *(2)*

b) Describe the arrangement of atoms

i) around the carbon atom in urea

ii) around a nitrogen atom in urea. *(2)*

c) Suggest two advantages of using urea as a fertiliser compared with ammonium nitrate. *(2)*

13 When space travel was being pioneered, one of the first rocket fuels was hydrazine, H_2NNH_2.

a) Draw a dot-and-cross diagram to show the electron structure of a hydrazine molecule. *(2)*

b) Predict the size of the H−N−H bond angle in a hydrazine molecule and explain your reasoning. *(3)*

c) Suggest a possible equation for the reaction which occurs when hydrazine vapour burns in oxygen. *(2)*

d) When 1.00 g of hydrazine burns in excess oxygen, 18.3 kJ of thermal energy is released. Calculate the enthalpy change of combustion of hydrazine. *(2)*

14 a) Draw a dot-and-cross diagram for methylamine, CH_3NH_2. *(1)*

b) Give approximate values for the H−C−H and C−N−H bond angles in methylamine. Explain your answer. *(5)*

c) Amines such as methylamine form hydrogen bonds with each other. Using displayed formulae, draw a diagram to show the hydrogen bond between two methylamine molecules and give the bond angle around the shared hydrogen atom. *(3)*

d) i) Write the formula of the compound formed when methylamine reacts with hydrogen chloride. *(1)*

ii) Give the C−N−H bond angle in this product and explain your answer. *(2)*

15 Predict three possible arrangements of bonds for the ICl_3 molecule. By considering the electron-pair repulsions in each of your structures, suggest which is the most likely shape and justify your answer. *(9)*

16 Explain why the melting temperatures of the Group 7 elements rise down the group, but the melting temperatures of the Group 1 elements fall down the group. *(6)*

17 Thin streams of some liquids are attracted towards a charged rod, but with other liquids there is no effect.

a) Explain why some liquids are attracted while others are not. *(2)*

b) Predict which of the following liquids are deflected towards a charged rod and explain your predictions: water, hexane, bromoethane, tetrachloromethane. *(4)*

c) Why are the affected liquids always attracted towards the charged rod and not repelled? *(2)*

Substance	Melting temperature/°C	Boiling temperature/°C	Electrical conductivity as solid	Electrical conductivity as liquid	Electrical conductivity in water
A	−113	101	Poor	Poor	Insoluble
B	1510	2370	Good	Good	Insoluble
C	1020	1660	Poor	Good	Good
D	1883	2503	Poor	Poor	Insoluble
E	−88	−67	Poor	Poor	Good
F	2072	2980	Poor	Good	Insoluble
G	−39	357	Good	Good	Insoluble

18 a) Use the information in the table above to deduce the bonding (ionic, covalent or metallic) in the following substances and whether they exist as giant lattices or small molecules or neither. *(7)*

b) Given that the seven substances are aluminium oxide, 1-bromobutane, hydrogen bromide, manganese, mercury, silicon dioxide and sodium bromide, assign a letter to each. *(7)*

19 Suggest explanations for each of the following:

a) Sodium has a higher melting temperature than potassium. *(4)*

b) Magnesium oxide has a higher melting temperature than magnesium chloride. *(3)*

c) The boiling temperature of chlorine is 238 K, but temperatures in excess of 1300 K are needed to form chlorine atoms from chlorine molecules. *(4)*

d) When aluminium chloride is heated, it sublimes at 451 K to form vapour which contains Al_2Cl_6 molecules. *(4)*

20 The enthalpy change of vaporisation of a liquid is a measure of the strength of its intermolecular forces. The table shows values for the enthalpy change of vaporisation of the hydrides of Group 6 elements.

Compound	$\Delta H_{\text{vaporisation}}$/ kJ mol^{-1}
H_2O	40.7
H_2S	18.7
H_2Se	19.3
H_2Te	23.2

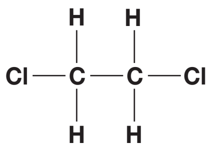
a) Plot a graph of $\Delta H_{\text{vaporisation}}$ against molar mass for the four compounds. *(4)*

b) What types of intermolecular forces are there between the molecules of H_2S and between molecules of H_2Se? *(1)*

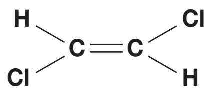
c) Use your graph to estimate the value $\Delta H_{\text{vaporisation}}$ for water, assuming that the only intermolecular forces in water are the same as in the other hydrides in Group 6. *(1)*

d) Use your graph and the answer to c) to estimate the strength of hydrogen bonding in water. *(1)*

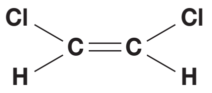
21 Consider the following three molecules:



1,2-dichloroethane



E-1,2-dichloroethene



Z-1,2-dichloroethene

(IUPAC names of organic molecules such as these are studied in Chapter 6.1.)

Deduce whether each molecule has an overall dipole and justify your answer. *(6)*

22 Hydrogen reacts with sodium to form sodium hydride, an ionic compound which has the same lattice structure as sodium chloride.

a) i) Write an equation, including state symbols, for the formation of sodium hydride from its elements. *(2)*

ii) Draw dot-and-cross diagrams for the ions in sodium hydride showing the outer electrons and the ionic charges. *(2)*

b) Electrolysis of sodium hydride dissolved in molten sodium chloride produces hydrogen. State at which electrode hydrogen is discharged and write a half-equation for the formation of hydrogen in this electrolysis. *(2)*

c) Unlike sodium chloride, sodium hydride does not simply dissolve in water, but reacts with water to form a strongly alkaline solution.

Write an equation for the reaction of the hydride ion with water and state the role of the hydride ion in this reaction. *(2)*

d) Magnesium hydride has been suggested as a medium for the storage of hydrogen. Comment on the likely bonding in magnesium hydride and suggest two possible ways to release hydrogen from magnesium hydride. *(4)*

● **23 a)** Benzenecarboxylic acid (C_6H_5COOH) is almost insoluble in cold water; only 2.9 g dissolves in 1 dm^3 water at 25 °C.

However about 70 g of the acid will dissolve in 1 dm^3 of tetrachloromethane at 25 °C. In this solution, the solute particles are dimers of benzenecarboxylic acid.

i) Explain why, at 25 °C, benzenecarboxylic acid is much more soluble in tetrachloromethane than in water. *(2)*

ii) Draw a structure for the dimer of benzenecarboxylic acid formed in tetrachloromethane and suggest how and why it forms. *(4)*

b) A conical flask contains 2.90 g of benzenecarboxylic acid. Aqueous sodium hydroxide solution is added from a burette and the mixture shaken until a colourless solution is formed.

i) Write an equation for the reaction of sodium hydroxide with benzenecarboxylic acid. *(1)*

ii) Calculate the volume of 0.500 $mol\,dm^{-3}$ sodium hydroxide needed to react exactly with 2.90 g of benzenecarboxylic acid. *(3)*

iii) Explain why the organic product of the reaction is very soluble in water. *(2)*

● **24** The boiling temperatures of five compounds are shown in the table.

Name	Formula	Boiling temperature/°C
Water	H_2O	100
Methanol	CH_3OH	65
Ammonia	NH_3	−33
Ethanamide	CH_3CONH_2	221
Ethanoic acid	CH_3COOH	118

a) Explain why the boiling temperature of water is higher than that of methanol and much higher than that of ammonia. *(6)*

b) Consider the structures of ethanamide and ethanoic acid and suggest why the boiling temperature of ethanamide is higher than that of ethanoic acid. *(4)*

NOTE: Part (b) requires study beyond AS Level.

● **25** The electronegativity value of tin is 1.8. Tin reacts with fluorine to form a fluoride which contains 61.0% of tin and which has a melting temperature of 705 °C. Tin also reacts with iodine to form an iodide which contains 19.0% of tin and which has a melting temperature of 144 °C. Use other electronegativity values from Table 2.5 to help you discuss the bonding types in these two tin halides. Suggest why the compounds are different. *(9)*

3

Redox I

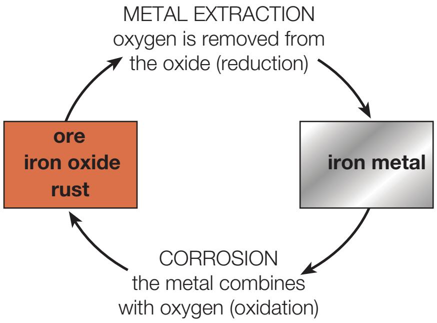

METAL EXTRACTION
oxygen is removed from the oxide (reduction)
ore
iron oxide
rust
iron metal
CORROSION
the metal combines with oxygen (oxidation)

Figure 3.1 The cycle of extraction and corrosion for iron.

3.1 Oxidation and reduction

Oxidation and reduction reactions are very common. Chemists have devised a number of ways of recognising and describing what happens during changes of this kind.

Burning is perhaps the commonest example of oxidation. Another example is rusting, which converts iron to a form of iron oxide. At its simplest, oxidation involves adding oxygen to an element or compound.

Reduction is the opposite of oxidation. Metal oxides are reduced during the extraction of metals from their ores. In a blast furnace, for example, carbon monoxide takes the oxygen away from iron oxide to leave metallic iron (Figure 3.1).

Tip

The elements oxygen and hydrogen can be regarded as chemical opposites in oxidation and reduction reactions. Older definitions also defined oxidation at the loss of hydrogen and reduction as the gain of hydrogen. Defining oxidation and reduction in terms of the loss or gain of hydrogen is now rarely used, except in organic chemistry.

Test yourself

1 In terms of gain or loss of oxygen, which element or compound is oxidised and which is reduced in the reaction of:

- **a)** steam with hot magnesium
- **b)** copper(II) oxide with hydrogen
- **c)** aluminium with iron(III) oxide
- **d)** carbon dioxide with carbon to form carbon monoxide?

3.2 Equations to explain oxidation and reduction reactions

Balanced symbol equations

Chemists write equations, with symbols and formulae, to describe and explain what happens during reactions. Writing a word equation is a useful first step towards a balanced chemical equation with symbols. This is because it is not possible to write an equation without first knowing the identity of the reactants and products. Figure 3.2 shows sparks from a sparkler – these sparks are bits of burning magnesium. When magnesium burns in air, it reacts with oxygen to form white magnesium oxide.

Figure 3.2 When sparklers burn, bits of magnesium react with oxygen in the air.

Example

Write a balanced equation for the reaction of magnesium with oxygen.

Notes on the method

There are four key steps in writing an equation. Before writing the equation you must identify the reactants and the products.

Oxygen, hydrogen, nitrogen and the halogens are diatomic molecules with two atoms in their molecules – so they are written as O_2, H_2, N_2, F_2, Cl_2, Br_2 and I_2. There are some other molecular non-metals but most other elements are shown as single atoms.

Never change a formula to make an equation balance. The formula of magnesium oxide is always MgO and never MgO_2 or Mg_2O, or anything else for that matter.

Answer

Step 1: Write a word equation for the reaction.

magnesium + oxygen → magnesium oxide

Step 2: Write symbols for the elements and formulae for the compounds in the word equation.

$$Mg + O_2 \rightarrow MgO$$

Step 3: Balance the equation by putting numbers in front of the symbols and formulae, so that the number of each type of atom is the same on both sides of the equation.

$$2Mg + O_2 \rightarrow 2MgO$$

Step 4: Add state symbols to show the state of each substance in the equation. Use (s) for solid, (l) for liquid, (g) for gas and (aq) for an aqueous solution (a substance dissolved in water).

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

Test yourself

2 Write balanced equations, with state symbols, for these reactions:

a) steam with hot magnesium

b) copper(II) oxide with hydrogen

c) aluminium with iron(III) oxide

d) carbon dioxide with carbon to form carbon monoxide.

Balanced chemical equations are important because they:

- identify the reactants and products with their formulae
- indicate relative numbers of atoms and molecules in the reaction
- make it possible to calculate the amounts of the chemical substances involved (Chapter 5).

Electron transfer

The compound formed when magnesium burns in air is ionic. It is made up of magnesium ions, Mg^{2+}, and oxide ions, O^{2-}. During the reaction, each magnesium atom gives up two electrons, turning into a magnesium ion:

$$2Mg \rightarrow 2Mg^{2+} + 4e^-$$

Oxygen takes up the electrons from the magnesium producing oxide ions:

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

In this way, electrons transfer from magnesium atoms to oxygen atoms, forming ions from atoms.

Magnesium atoms also turn into ions when they react with other non-metals such as chlorine, bromine and sulfur. In all its reactions with non-metals, magnesium loses electrons and its atoms become positive ions. The atoms of the non-metal gain electrons and become negative ions. So all the reactions involve electron transfer (Figure 3.3). Magnesium is oxidised as it loses electrons; the non-metal is reduced as it gains electrons. Reduction and oxidation go together in these **redox reactions**.

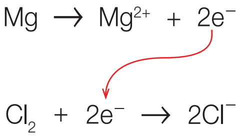

$Mg \rightarrow Mg^{2+} + 2e^-$
$Cl_2 + 2e^- \rightarrow 2Cl^-$

Figure 3.3 Electron transfer in the reaction of magnesium with chlorine.

Table 3.1 The charges on common ions.

Positive ions (cations)			Negative ions (anions)		
Charge	**Cation**	**Symbol**	**Charge**	**Anion**	**Symbol**
1+	Sodium	Na^+	1–	Chloride	Cl^-
	Potassium	K^+		Bromide	Br^-
	Silver	Ag^+		Iodide	I^-
	Copper(I)	Cu^+		Hydroxide	OH^-
	Hydrogen	H^+		Nitrite	NO_2^-
	Ammonium	NH_4^+		Nitrate	NO_3^-
2+	Magnesium	Mg^{2+}	2–	Oxide	O^{2-}
	Calcium	Ca^{2+}		Sulfide	S^{2-}
	Zinc	Zn^{2+}		Sulfite	SO_3^{2-}
	Copper(II)	Cu^{2+}		Sulfate	SO_4^{2-}
	Iron(II)	Fe^{2+}		Carbonate	CO_3^{2-}
3+	Aluminium	Al^{3+}	3–	Nitride	N^{3-}
	Iron(III)	Fe^{3+}		Phosphate	PO_4^{3-}

Notice from Table 3.1 that:

- metal ions are always positive
- non-metal ions are negative except hydrogen, H^+, and ammonium, NH_4^+
- some metals can form more than one ion – this is characteristic of metals in the d block such as copper and iron
- some non-metal ions are compound ions containing more than one kind of atom, including **oxoanions** such as the sulfate, nitrate and phosphate ions.

Ionic half-equations

A **half-equation** is used to describe either the gain or the loss of electrons during a redox process. Half-equations help to show what is happening during a reaction. Two half-equations combine to give the overall balanced equation.

Zinc metal can reduce copper ions to copper. This happens when pieces of zinc are added to a solution of copper(II) sulfate (Figure 3.4). In this example of a **displacement reaction** the more reactive metal, zinc, displaces the less reactive metal, copper. The reaction can be shown as two half-equations:

electron gain (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

electron loss (oxidation): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Tip

You may find the mnemonic, **oil rig** helpful when thinking about redox in terms of the loss or gain of electrons.

Oxidation	**R**eduction
Is	**I**s
Loss	**G**ain

Key terms

A **redox reaction** is a reaction that involves **red**uction and **ox**idation.

An **oxoanion** is an ion with the general formula is $X_xO_y^{z-}$ (where X represents any element while O represents an oxygen atom). Metals and non-metal elements form oxoanions. The oxoanions of non-metals shown in Table 3.1 are particularly common.

A **half-equation** is an ionic equation used to describe either the gain, or the loss, of electrons during a redox reaction.

Displacement reactions are redox reactions which can be used to compare the relative strengths of metals as reducing agents and non-metals as oxidising agents. A more reactive metal displaces a less reactive metal from one of its salts.

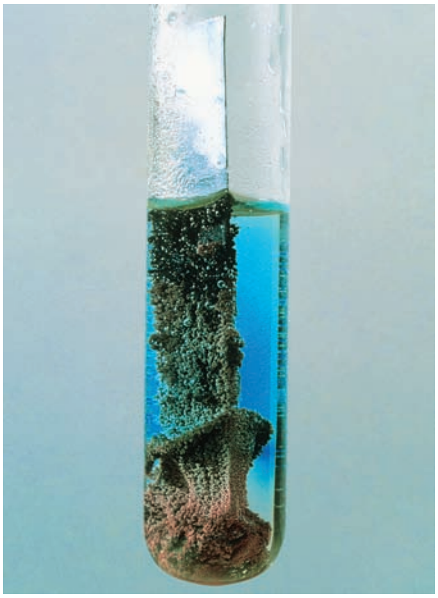


Figure 3.4 Zinc displacing copper from copper(II) sulfate solution. The copper appears as a reddish solid. Colourless zinc ions replace the copper ions in solution.

Key terms

Spectator ions are ions which are present in solution but take no part in a reaction.

Ionic equations describe chemical changes by showing only the reacting ions and any other reacting atoms or molecules, while leaving out the spectator ions (Section 4.1).

Oxidation originally meant combination with oxygen, but the term now covers all reactions in which atoms, molecules or ions lose electrons. The definition is extended to cover molecules, as well as atoms and ions, by defining oxidation as a change which makes the oxidation number of an element more positive, or less negative.

Reduction originally meant removal of oxygen or addition of hydrogen, but the term now covers all reactions in which atoms, molecules or ions gain electrons. The definition is extended to cover molecules, as well as atoms and ions, by defining reduction as a change which makes the oxidation number of an element more negative, or less positive.

Note that the sulfate ions in copper(II) sulfate are not shown. They are left out of the half-equation because they are the same before and after the reaction. For this reason they are called **spectator ions**. For clarity and simplicity, chemists often omit spectator ions from equations.

Adding together the two half-equations leads to the full **ionic equation**. The electrons must cancel in order that the electrons gained on one side of the equation equal the electrons lost on the other side. It is sometimes necessary to multiply one of the half-equations by a factor of two or three such that the electrons gained and lost are equal.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

Test yourself

3 With the help of Table 3.1, write the separate ionic half-equations for the reactions of:

a) sodium with chlorine

b) zinc with oxygen

c) calcium with bromine.

4 Write the ionic half-equations and the full ionic equation for the reaction of zinc with silver nitrate solution.

3.3 Oxidation numbers

Chemists use oxidation numbers to keep track of the electrons transferred or shared during chemical changes. With the help of oxidation numbers it becomes much easier to recognise redox reactions. Oxidation numbers also provide a useful way of organising the chemistry of elements such as chlorine, which can be oxidised or reduced to varying degrees. Chemists base the names of inorganic compounds on oxidation numbers.

Oxidation numbers and ions

Oxidation numbers show how many electrons are gained or lost by an element when atoms turn into ions and vice versa. In Figure 3.5, movement up the diagram involves the loss of electrons and a shift to more positive oxidation numbers – this is **oxidation**. Movement down the diagram involves the gain of electrons and a shift to less positive, or more negative, oxidation numbers – this is **reduction**.

The oxidation number of all uncombined elements is zero. In a simple ion, the oxidation number of the element is the charge on the ion. For example, in calcium chloride the metal is present as the Ca^{2+} ion and the oxidation number of calcium is +2.

Oxidation numbers distinguish between the compounds of elements such as iron that can exist in more than one oxidation state. In iron(II) chloride the Roman number 'II' shows that iron is in oxidation state +2. Iron atoms lose two electrons when they react with hydrogen chloride to make iron(II) chloride.

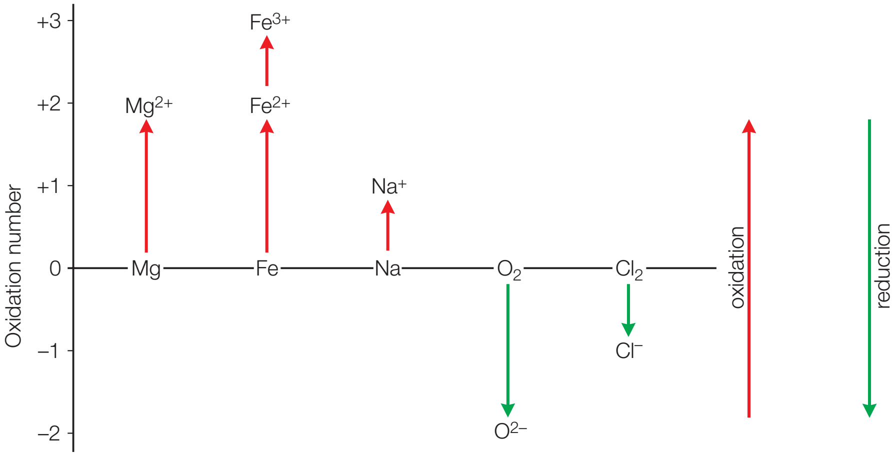


Figure 3.5 Oxidation numbers of atoms and ions.

Tip

It is ambiguous just to state that oxidation numbers get higher or lower because both positive and negative numbers are involved. To be clear, state that during oxidation the oxidation number of an element gets more positive, or less negative; while during reduction the oxidation number of an element gets less positive, or more negative.

Oxidation number rules

1. The oxidation number of uncombined elements is zero.
2. In ions made of just one atom the oxidation number of the element is the charge on the ion.
3. The sum of the oxidation numbers in a neutral compound is zero.
4. The sum of the oxidation numbers for an ion is the charge on the ion.
5. Some elements have fixed oxidation numbers in all their compounds.

Metals		**Non-metals**	
Group 1 metals (e.g. Li, Na, K)	+1	hydrogen (except in metal hydrides, H^-)	+1
Group 2 metals (e.g. Mg, Ca, Ba)	+2	fluorine	−1
aluminium	+3	oxygen (except in peroxides, O_2^{2-}, and compounds with fluorine)	−2
		chlorine (except in compounds with oxygen and fluorine)	−1

Figure 3.6 Oxidation number rules.

NH_4^+
−3 +1

MnO_4^-
+7 −2

SO_4^{2-}
+6 −2

$Cr_2O_7^{2-}$
+6 −2

Figure 3.7 Oxidation numbers in ions with more than one atom. Note the use of 2− for the electric charge on a sulfate ion (number first for ionic charges) but the use of −2 to refer to the oxidation state of oxygen in the ion (plus or minus first for oxidation states in ions and molecules).

With the help of the rules in Figure 3.6, it is possible to extend the use of oxidation numbers to ions consisting of more than one atom. The charge on an ion, such as the sulfate ion, is the sum of the oxidation numbers of the atoms. The normal oxidation state of oxygen is −2. There are four oxygen atoms (four at −2) in the sulfate ion, so the oxidation state of sulfur must be +6 to give an overall charge on the ion of −2 (Figure 3.7).

Care is necessary when assigning oxidation numbers in ions where there are covalent bonds between same element. The formula of the peroxide ion, O_2^{2-}, for example is:

$[O{-}O]^{2-}$

In this ion the oxidation number of each oxygen atom is −1 (and not −2 as usual). This follows from the rule that the sum of the oxidation numbers adds up to the charge on the ion.

Oxidation numbers and molecules

The rules in Figure 3.6 make it possible to apply the definitions of oxidation and reduction to molecules. In most molecules, the oxidation state of an atom corresponds to the number of electrons from that atom that are shared in covalent bonds (Figure 3.8).

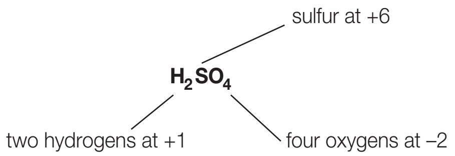


Figure 3.8 Oxidation numbers of the elements in sulfuric acid.

Where two atoms are linked by covalent bonds, the more electronegative atom (Section 2.5) has the negative oxidation state. Fluorine always has a negative oxidation state of −1 because it is the most electronegative of all atoms. Oxygen normally has a negative oxidation state (−2) but it has a positive oxidation state (+1) when combined with fluorine.

Tip

Oxidation numbers are written with the + or − in front of the number: +1, +2 or −1, −2. This is to make it quite clear that when dealing with molecules these numbers do not refer to electric charges, unlike charges on ions such as Ca^{2+} or N^{3-}. Molecules are not charged. The sum of the oxidation states for all the atoms in a molecule is zero.

Test yourself

5 What is the oxidation number of:

a) aluminium in aluminium oxide, Al_2O_3

b) nitrogen in magnesium nitride, Mg_3N_2

c) nitrogen in barium nitrate, $Ba(NO_3)_2$

d) nitrogen in the ammonium ion, NH_4^+?

6 Are these elements oxidised or reduced when they react to form these compounds?

a) calcium to calcium bromide

b) chlorine to lithium chloride

c) chlorine to chlorine dioxide

d) sulfur to hydrogen sulfide

e) sulfur to sulfuric acid

Oxidation numbers and the chemistry of elements

Oxidation numbers help to make sense of the chemistry of an element such as bromine (see Figure 3.9). The compounds of an element can be classified according to their **oxidation states**.

Key term

Oxidation states are the states of oxidation, or reduction, shown by an element in its chemistry. The states are labelled with the oxidation numbers of the element in that state.

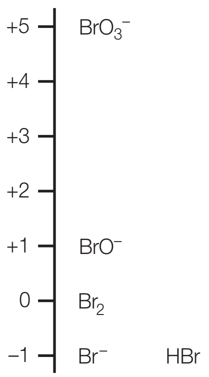


Figure 3.9 Bromine is reduced when it reacts to form bromide ions. A reaction turning bromine into BrO^- ions involves oxidation of bromine. The conversion of BrO^- ions to BrO_3^- ions involves further oxidation of bromine.

The oxidation numbers of the elements lithium to chlorine in their oxides reveal a periodic pattern when plotted against atomic number (Figure 3.10). The most positive oxidation number for each element corresponds to the number of electrons in the outer shell of the atoms.

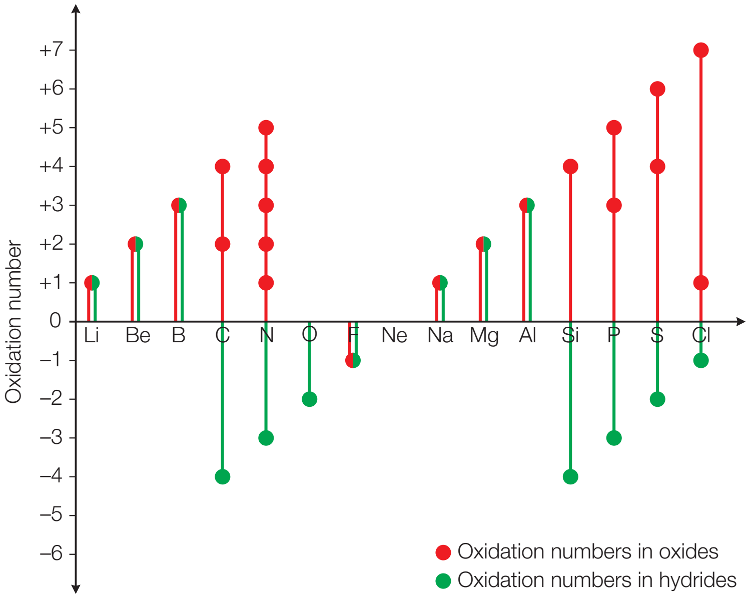


Figure 3.10 Oxidation numbers of elements in their oxides and hydrides. Note that some elements form oxides in a variety of oxidation states.

Test yourself

7 This question refers to Figure 3.10.

a) Give the formula of the oxide of lithium.

b) Give the formulae of the two oxides of carbon.

c) What are the oxidation states of nitrogen in these oxides: NO, N_2O, NO_2, N_2O_3, N_2O_5?

d) Give the formulae of the hydrides of nitrogen and phosphorus.

e) Why is there only one element with a negative oxidation number in an oxide?

Oxidation numbers and the names of compounds

The names of inorganic compounds are becoming increasingly systematic, but chemists still use a mixture of names. Most prefer the name ‘copper sulfate’ for the blue crystals with the formula $CuSO_4.5H_2O$. This is hydrated copper(II) sulfate. Its fully systematic name, tetraaquocopper(II) tetraoxosulfate(VI)-1-water, is rarely used. This fully systematic name has much more to say about the arrangement of atoms, molecules and ions in the blue crystals but it is too cumbersome for normal use. The fully systematic name also shows the oxidation states of copper and sulfur in the compound.

Here are some of the basic rules for naming common inorganic compounds:

- the ending '-ide' shows that a compound contains just the two elements mentioned in the name. The more electronegative element comes second – for example, sodium sulfide, Na_2S, carbon dioxide, CO_2, and magnesium nitride, Mg_3N_2
- the Roman numbers in names indicate the oxidation numbers of the elements – for example iron(II) sulfate, $FeSO_4$, and iron(III) sulfate, $Fe_2(SO_4)_3$
- the traditional names of oxoacids end in '-ic' or '-ous' as in sulfuric acid, H_2SO_4, and sulfurous acid, H_2SO_3, as well as in nitric acid, HNO_3, and nitrous acid, HNO_2. The '-ic' ending is for the acid in which the central atom has the higher oxidation number
- the corresponding traditional endings for the salts of oxoacids are '-ate' and '-ite' as in sulfate, SO_4^{2-}, and sulfite, SO_3^{2-}, and in nitrate, NO_3^-, and nitrite, NO_2^-
- the more systematic names for oxoacids and oxosalts use oxidation numbers as in sulfate(VI) for sulfate, SO_4^{2-}, sulfate(IV) for sulfite, SO_3^{2-}, as well as nitrate(V) for nitrate and nitrate(III) for nitrite.

When in doubt, chemists give the name and the formula. In some cases, they may give two names – the systematic name and the traditional name.

Tip

In practice, the oxidation number for metals is always given in names where it can vary, but the oxidation number for the element in common oxoanions is less often given. So the name iron(III) nitrate is regularly used rather than iron(III) nitrate(V); similarly copper(II) sulfate is much more common than copper(II) sulfate(VI).

Test yourself

8 Write the formulae of the compounds:

a) tin(II) oxide

b) tin(IV) oxide

c) iron(III) nitrate(V)

d) potassium sulfate(VI).

3.4 Recognising redox reactions

Oxidation numbers help us to identify redox reactions. In the equation for any redox reaction, at least one element changes to a more positive oxidation state, while another changes to a less positive oxidation state. A reaction is not a redox reaction if there are no changes of oxidation state.

Oxidising and reducing agents

An agent is someone or something which gets things done. In spy stories, the main players are secret agents with a mission to make a change. In redox reactions, the chemicals with a mission are the oxidising and reducing agents.

The term 'oxidising agent' (or oxidant) describes chemical reagents which can oxidise other atoms, molecules or ions by taking electrons away from them. Common oxidising agents are oxygen, chlorine, nitric acid, potassium manganate(VII), potassium dichromate(VI) and hydrogen peroxide.

The term 'reducing agent' (or reductant) describes chemical reagents which can reduce other atoms, molecules or ions by giving them electrons. Common reducing agents are hydrogen, sulfur dioxide and zinc or iron in acid.

It is easy to get into a mental tangle when using these terms. An oxidising agent reacts by removing electrons from the reducing agent. The oxidising agent gains electrons and so is reduced, the reducing agent loses electrons and so is oxidised (Figure 3.11).

Tip

Fluorine is a very powerful oxidising agent but it is much too reactive and dangerous for normal use.

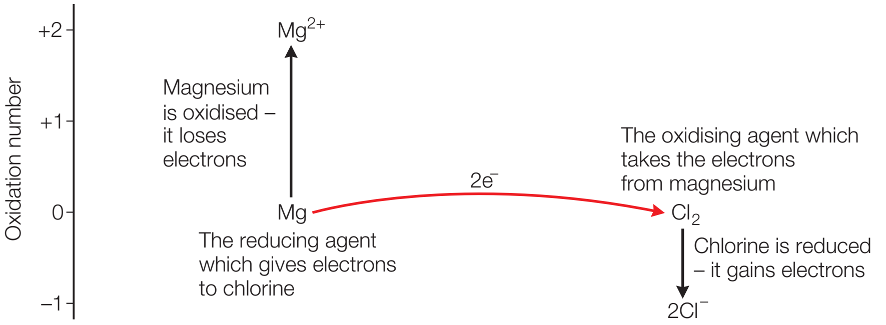

Oxidation number
+2
+1
0
−1
Mg²⁺
Magnesium is oxidised – it loses electrons
Mg
The reducing agent which gives electrons to chlorine
2e⁻
The oxidising agent which takes the electrons from magnesium
Cl₂
Chlorine is reduced – it gains electrons
2Cl⁻

Figure 3.11 Magnesium is oxidised by loss of electrons. It is oxidised by chlorine, so chlorine is the oxidising agent. At the same time chlorine gains electrons and is reduced by magnesium. Magnesium is the reducing agent.

Disproportionation reactions

In some reactions, the same element both increases and decreases its oxidation number. In other words, some of the element is oxidised while the rest of it is reduced. This is called disproportionation. One example is the decomposition of hydrogen peroxide to oxygen and water.

$$2H_2O_2(aq) \rightarrow 2H_2O + O_2$$

$-1 \qquad\qquad -2 \qquad 0$

Half of the oxygen in hydrogen peroxide is reduced from the −1 to the −2 state in water, while the other half is oxidised from the −1 to the 0 state in oxygen gas.

Another example of a **disproportionation reaction** takes place on warming copper(I) oxide with dilute sulfuric acid. The reaction does not produce a solution of copper(I) sulfate. Instead, the products are a solution of copper(II) sulfate and a precipitate of copper metal.

$$Cu_2O(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + Cu(s) + H_2O(l)$$

$+1 \qquad\qquad\qquad\qquad +2 \qquad\qquad 0$

Half of the copper(I) is oxidised to copper(II), while the rest is reduced to copper(0). Reactions of this kind are important in the chemistry of the halogens (Section 4.11).

Key term

A **disproportionation reaction** involves an element in a single species being simultaneously oxidised and reduced.

Test yourself

9 Use oxidation numbers to show that these are disproportionation reactions.

a) $2CO(g) \rightarrow C(s) + CO_2(g)$

b) $3K_2MnO_4(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 2KMnO_4(aq) + 4KOH(aq)$

c) $2Ca(OH)_2(s) + 2Cl_2(aq) \rightarrow CaCl_2(aq) + Ca(ClO)_2(aq) + 2H_2O(l)$

3.5 Balancing redox equations

Balancing redox equations using half-equations

Half-equations can help to balance equations for redox reactions because the electrons lost when an atom, molecule or ion is oxidised in one half-equation have to equal the electrons gained by the reduction of another species in the second half-equation.

The half-equations in Section 3.2 only included atoms, ions and electrons. There are also redox half-equations for the reactions of molecules or ions that include oxygen such as the nitrate ion, hydrogen peroxide and sulfur dioxide. These chemicals often react in acid solutions and the half-equations are balanced by including hydrogen ions and water molecules.

Tip

A redox half-equation must include the substance being oxidised or reduced plus electrons. It may also include hydrogen ions (in acid solution) and water molecules.

Example

An acidic solution of chloric(I) acid, HOCl, is reduced to chloride ions as it oxidises iodide ions to iodine. What is the balanced equation for the reaction?

Notes on the method

You have to know, or be told, what the reactants and products are before you can write the equation for a reaction. You can then follow the five steps illustrated in this example. In acid solution you can only use water molecules or hydrogen ions to balance the half-equations for O and H.

You do not need to keep rewriting the equations so long as you leave spaces on each side to add the water molecules, hydrogen ions and electrons.

Answer

Step 1: Write down the given information about the half-equations, then balance the atoms being oxidised and reduced.

$$\begin{aligned} &\mathrm{HOCl(aq)} &&\rightarrow \mathrm{Cl^-(aq)} \\ &\mathrm{2I^-(aq)} &&\rightarrow \mathrm{I_2(aq)} \end{aligned}$$

Step 2: Balance the hydrogen and oxygen atoms by adding H_2O and/or H^+ (in acid solution).

$$\begin{aligned} &\mathrm{HOCl(aq) + H^+(aq)} &&\rightarrow \mathrm{Cl^-(aq) + H_2O(l)} \\ &\mathrm{2I^-(aq)} &&\rightarrow \mathrm{I_2(aq)} \end{aligned}$$

Step 3: Balance the electric charges by adding electrons.

$$\begin{aligned} &\mathrm{HOCl(aq) + H^+(aq) + 2e^-} &&\rightarrow \mathrm{Cl^-(aq) + H_2O(l)} \\ &\mathrm{2I^-(aq)} &&\rightarrow \mathrm{I_2(aq) + 2e^-} \end{aligned}$$

Step 4: If necessary, multiply one half-equation so that the numbers of electrons in each are the same, then add them, cancelling the electrons (in this example the numbers of electrons in each are already the same).

$$\begin{aligned} &\mathrm{HOCl(aq) + H^+(aq) + 2e^-} &&\rightarrow \mathrm{Cl^-(aq) + H_2O(l)} \\ &\mathrm{2I^-(aq)} &&\rightarrow \mathrm{I_2(aq) + 2e^-} \\ \hline &\mathrm{HOCl(aq) + H^+(aq) + 2I^-(aq)} &&\rightarrow \mathrm{Cl^-(aq) + H_2O(l) + I_2(aq)} \end{aligned}$$

Step 5: If necessary, simplify the equation by cancelling molecules or ions that appear on both sides of the equation (not needed in this example).

Test yourself

10 Use half-equations to write balanced ionic equations for these redox reactions.

a) H_2O_2 with Fe^{2+} to give H_2O and Fe^{3+}

b) SO_3^{2-} and Cl_2 to give SO_4^{2-} and Cl^-.

c) the disproportionation of IO^- into I^- and IO_3^-

Balancing redox equations using oxidation numbers

Oxidation numbers offer an alternative way to balance redox equations. This is because the total decrease in oxidation number for the element that is reduced must equal the total increase in oxidation number for the element that is oxidised.

Example

What is the balanced equation for the reaction of concentrated sulfuric acid with hydrogen bromide? The products are bromine, sulfur dioxide and water.

Notes on the method

You have to know, or be told, what the reactants and products are before you can write the equation for a reaction. You can then follow the five steps illustrated in this example.

Answer

Step 1: Write down the formulae for the atoms, molecules and ions involved in the reaction.

$$HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + H_2O$$

Step 2: Identify the elements which change in oxidation number and the extent of change.
In this example only bromine and sulfur show changes of oxidation state.

Step 3: Balance so that the total increase in oxidation number of one element equals the total decrease of the other element.
In this example, the increase of +1 in the oxidation number of two bromine atoms (from −1 to 0) balances the −2 decrease of one sulfur atom (from +6 to +4).

$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + H_2O$$

Step 4: Balance for oxygen and hydrogen.
In this example, the four hydrogen atoms on the left of the equation join with the two remaining oxygen atoms to form two water molecules.

$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$$

Step 5: Add the state symbols.

$$2HBr(g) + H_2SO_4(l) \rightarrow Br_2(l) + SO_2(g) + 2H_2O(l)$$

Test yourself

11 Use oxidation numbers to write the full ionic equation for each of these redox reactions.

State which element is oxidised and which is reduced in each example.

- **a)** Fe with Br_2 to give $FeBr_3$
- **b)** F_2 with H_2O to give HF and O_2
- **c)** IO_3^- and H^+ with I^- to give I_2, and H_2O
- **d)** $S_2O_3^{2-}$ and I_2 to give $S_4O_6^{2-}$ and I^-

Activity

Preparing a sample of an oxide of nitrogen

Lead(II) nitrate decomposes on heating to form three products. These are lead(II) oxide, nitrogen dioxide and oxygen. Nitrogen dioxide, NO_2, is a brown gas. Some of the nitrogen dioxide molecules pair up to form N_2O_4. Cooling the gas mixture condenses the N_2O_4 as a greenish liquid (Figure 3.12).

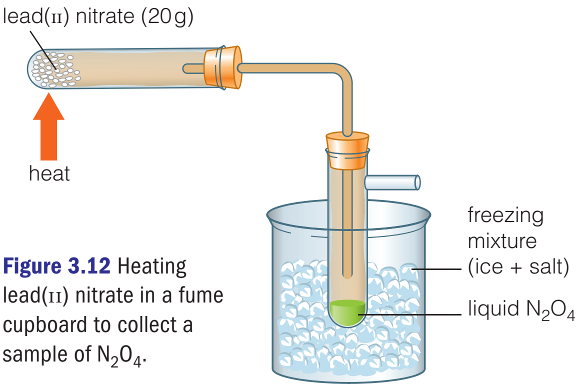


Figure 3.12 Heating lead(II) nitrate in a fume cupboard to collect a sample of N_2O_4.

1 Give the oxidation states of all the elements in:
a) lead(II) nitrate **b)** lead(II) oxide
c) nitrogen dioxide **d)** N_2O_4
e) oxygen gas.

2 Identify as oxidation, reduction or neither, the formation of:
a) lead(II) oxide from lead(II) nitrate
b) nitrogen dioxide from lead(II) nitrate
c) oxygen from lead(II) nitrate
d) N_2O_4 from NO_2.

3 Write balanced equations for:
a) the decomposition of lead(II) nitrate
b) the formation of N_2O_4 from NO_2.

4 Calculate the theoretical mass of N_2O_4 that could be collected by condensing the gases given off when 20 g lead(II) nitrate decomposes (Section 5.4).

5 Suggest reasons why the mass of N_2O_4 collected by heating 20 g lead(II) nitrate in the apparatus in Figure 3.12 is less than your answer to Question 4.

Exam practice questions

1 These are incomplete half-equations for changes involving reduction in solution. Complete and balance the half-equations.
a) $H^+(aq) \rightarrow H_2(g)$ *(1)*
b) $Fe^{3+}(aq) \rightarrow Fe^{2+}(aq)$ *(1)*
c) $H_2O_2(aq) + 2H^+(aq) \rightarrow 2H_2O(l)$ *(1)*

2 These are incomplete half-equations for changes involving oxidation in solution. Complete and balance the half-equations.
a) $Mg(s) \rightarrow Mg^{2+}(aq)$ *(1)*
b) $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq)$ *(1)*
c) $I^-(aq) \rightarrow I_2(aq)$ *(1)*

3 Select a reduction from Question 1 and an oxidation from Question 2 and combine them to give the full ionic equation for these reactions:
a) iron(III) ions with tin(II) ions *(2)*
b) magnesium with dilute hydrochloric acid *(2)*
c) hydrogen peroxide with iodide ions. *(2)*

4 What are the oxidation numbers of chlorine in these ions: Cl^-, ClO^-, ClO_2^-, ClO_3^-, ClO_4^-? *(3)*

5 What are the oxidation numbers of nitrogen in these molecules: N_2, NH_3, N_2H_4, HNO_3, HNO_2, NH_2OH, NF_3? *(4)*

6 Write half-equations for these changes in solution – in each case state whether the process is an example of oxidation or of reduction:
a) cobalt(II) ions turning into cobalt(III) ions *(2)*
b) sulfur dioxide molecules in acid solution turning into hydrogen sulfide molecules *(2)*
c) hydroxide ions turning into oxygen and water molecules *(2)*
d) hydrogen molecules turning into hydrogen ions. *(2)*

7 Identify the element that disproportionates in each of these reactions by giving the oxidation states of the element before and after reaction:

a) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ *(2)*

b) $Cl_2(aq) + 2NaOH(aq)$
$\rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$ *(2)*

c) $3MnO_4^{2-}(aq) + 4H^+(aq)$
$\rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2H_2O(l)$ *(2)*

8 Rewrite each of these full ionic equations as two half-equations. In each case state which element has been oxidised and which has been reduced.

a) $2Fe^{2+}(aq) + Br_2(aq)$
$\rightarrow 2Fe^{3+}(aq) + 2Br^-(aq)$ *(3)*

b) $2I^-(aq) + Cl_2(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$ *(3)*

c) $Zn(s) + 2V^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2V^{2+}(aq)$ *(2)*

9 Balance these redox equations:

a) $CuO(s) + NH_3(g)$
$\rightarrow N_2(g) + H_2O(l) + Cu(s)$ *(2)*

b) $KI(s) + H_2SO_4(l)$
$\rightarrow K_2SO_4(s) + I_2(s) + H_2S(g) + H_2O(l)$ *(2)*

c) $NaIO_3(aq) + NaI(aq) + H_2SO_4(aq)$
$\rightarrow I_2(aq) + H_2O(l) + Na_2SO_4(aq)$ *(2)*

d) $Cu(s) + HNO_3(aq)$
$\rightarrow Cu(NO_3)_2(aq) + NO_2(g) + H_2O(l)$ *(2)*

10 Identify the atoms, molecules or ions that are oxidised and reduced in each of these reactions, stating the changes in oxidation number. In each case, write a full balanced equation for the reaction.

a) Hydrogen bromide gas reacts with sulfuric acid to form bromine and sulfur dioxide. *(3)*

b) An acidic solution of manganate(VII) ions, MnO_4^-, reacts with aqueous iron(II) ions. *(3)*

c) A sample of sodium chromate(VI) is made by the reaction of a chromium(III) salt with hydrogen peroxide in alkaline solution. *(3)*

d) An acidic solution of dichromate(VI) ions, $Cr_2O_7^{2-}$, is used to test for sulfur dioxide. When SO_2 is present, the solution turns green as Cr^{3+} ions form as well as sulfate ions. *(3)*

e) The reaction of gaseous hydrazine, N_2H_4, with gaseous dinitrogen tetroxide used to propel rockets in spacecraft producing nitrogen and steam in the exhaust gases. *(3)*

11 Briefly state four different definitions of the terms 'oxidation' and 'reduction'. *(4)*
Discuss the application of your definitions to these examples:

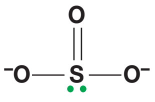
a) the reaction of hydrogen sulfide gas with moist sulfur dioxide to form sulfur and water *(4)*

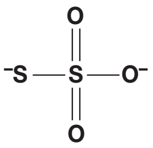
b) the reaction of hydrogen gas with hot sodium metal to form sodium hydride *(4)*

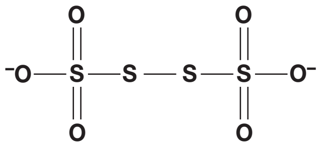
c) the reaction of hydrogen peroxide with potassium iodide in acid solution to form water and iodine *(4)*

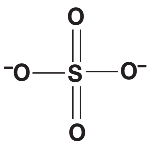
d) the decomposition of hydrogen peroxide to form oxygen and water. *(4)*

12 The diagram shows four oxoanions of sulfur.


sulfite ion


thiosulfate ion


tetrathionate ion


sulfate ion

a) What are the oxidation states of sulfur in the sulfite and the sulfate ions? What is the relationship, if any, between the oxidation numbers of sulfur in these two ions and the number of electrons used in bonding? *(4)*

b) A Level textbooks usually state that the oxidation number of sulfur in the thiosulfate ion is +2. However, some chemists suggest that that the two sulfur atoms in the ion have different oxidation states: −2 and +6. Similarly, the oxidation number in the tetrathionate ion is normally stated to be +2.5 in textbooks but in other sources the sulfur atoms are considered to be divided between the +6 and −1 states. Discuss the application of the oxidation number rules to:

- the thiosulfate ion
- the tetrathionate ion. *(6)*

c) Adding dilute hydrochloric acid to a solution of sodium thiosulfate produces a precipitate of sulfur and a solution of sulfur dioxide. Discuss the type of reaction taking place in terms of the alternative assignments of oxidation numbers suggested in (b). *(6)*

4

Inorganic chemistry and the periodic table

4.1 Types of inorganic reaction

Chemists classify the chemical reactions of inorganic elements and compounds in order to make sense of many thousands of reactions. By identifying the characteristics of similar reactions, chemists can predict how different substances will behave. Recognising and understanding the different types of reaction makes it possible to explain observations and to interpret the results of chemical tests.

Tip

Redox reactions are described in detail in Chapter 3. This section covers other types of inorganic reaction that are important in the study of groups in the periodic table.

Thermal decomposition

Compounds such as metal carbonates and metal nitrates may decompose when heated in a Bunsen flame. Green copper(II) carbonate, for example, breaks up on heating to form black copper(II) oxide and carbon dioxide. This is an example of **thermal decomposition**.

$$CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$$

Key term

Thermal decomposition is the name for a reaction in which a compound decomposes on heating.

Other metal carbonates, except those of most Group 1 metals, also decompose on heating. Carbonates of metals below copper in the reactivity series are so unstable that they cannot exist at room temperature.

Hydrated compounds like blue copper(II) sulfate, $CuSO_4.5H_2O$, contain water as part of their structure. They also decompose on heating. Fairly gentle heating causes most hydrates to give off water vapour, which often condenses to water on the cooler parts of the apparatus (Figure 4.1).

$$\underset{\text{blue hydrated copper(II) sulfate}}{CuSO_4.5H_2O(s)} \xrightarrow{\text{heat}} \underset{\text{white anhydrous copper(II) sulfate}}{CuSO_4(s)} + 5H_2O(g)$$

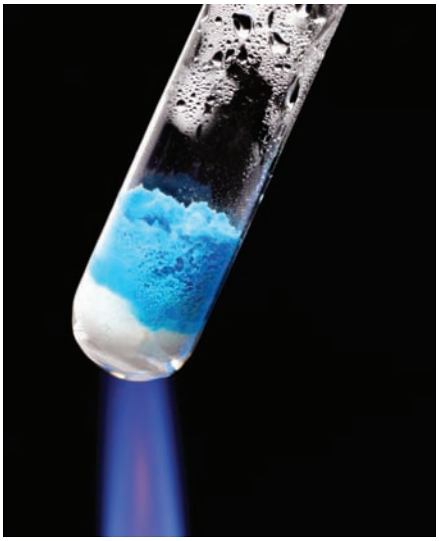


Figure 4.1 Copper(II) sulfate crystals decompose on heating to anhydrous copper(II) sulfate. The water driven off condenses on the cool part of the tube.

Test yourself

1 Some thermal decomposition reactions are also redox reactions. Use oxidation numbers to decide whether or not these examples of thermal decomposition are also redox reactions.

a) $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

b) $2Cu(NO_3)_2(s) \rightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$

c) $Ca(HCO_3)_2(s) \rightarrow CaO(s) + 2CO_2(g) + H_2O(l)$

d) $(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + N_2(g) + 4H_2O(l)$

Reactions of acids and alkalis

Acids and alkalis are commonly used as chemical reagents. Dilute hydrochloric acid is a convenient strong acid. Sodium hydroxide solution is often chosen as a strong base.

Acids do not simply mix with water when they dissolve in it – they react with it to produce aqueous hydrogen ions, $H^+(aq)$.

$$HCl(g) \xrightarrow{\text{water}} H^+(aq) + Cl^-(aq)$$

All acids produce $H^+(aq)$ ions with water and this is why dilute acids all react in a similar way. The typical reactions of dilute acids in water are the reactions of aqueous hydrogen ions. This makes it possible to rewrite the equations for the reactions of acids as **ionic equations** leaving out the **spectator ions**.

Key terms

Ionic equations describe chemical equations by showing only the reacting ions in solution while leaving out the spectator ions. Ionic equations are balanced both for atoms and for charges.

Spectator ions are ions which are present in solution but take no part in a reaction.

Acids reacting with metals

Acids react with the more reactive metals to form hydrogen gas plus an ionic metal compound called a salt (Figure 4.2).

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

The equation can be rewritten to show the ions in solution.

$$Mg(s) + 2H^+(aq) + \underset{\text{spectator ion}}{2Cl^-(aq)} \rightarrow Mg^{2+}(aq) + \underset{\substack{\text{spectator ion}\\\text{unchanged}}}{2Cl^-(aq)} + H_2(g)$$

The chloride ions are spectator ions so they can be left out of the ionic equation.

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

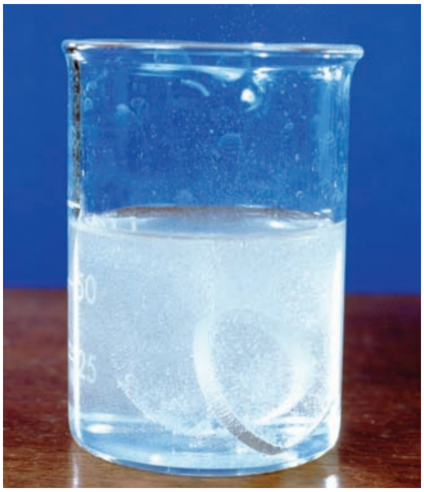


Figure 4.2 Bubbles of hydrogen forming as magnesium ribbon reacts with dilute hydrochloric acid. The magnesium atoms turn into ions and pass into solution where they mix with chloride ions to give a dilute solution of the salt magnesium chloride.

Acids reacting with metal oxides and hydroxides

All alkalis dissolve in water to produce hydroxide ions, OH^-. Sodium hydroxide (Na^+OH^-) and potassium hydroxide (K^+OH^-) contain hydroxide ions in the solid as well as in solution.

During a neutralisation reaction, an acid reacts with metal hydroxide, or metal oxide, to form a salt. Mixing the right amounts of dilute hydrochloric acid and sodium hydroxide solution, for example, produces a neutral solution of sodium chloride.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

This equation can also be rewritten to show the ions in solution:

$$H^+(aq) + \underbrace{Cl^-(aq) + Na^+(aq)}_{\text{spectator ions}} + OH^-(aq) \rightarrow \underbrace{Na^+(aq) + Cl^-(aq)}_{\substack{\text{spectator ions}\\\text{unchanged}}} + H_2O(l)$$

The sodium ions and chloride ions do not react. By cancelling the spectator ions, the equation simplifies to the ionic equation.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

This is true of all reactions between aqueous solutions of acids and alkalis. It shows that acids and alkalis neutralise each other because hydrogen ions react with hydroxide ions to form water.

Acids reacting with carbonates

Crystals of calcium carbonate consist of calcium and carbonate ions. The reaction with hydrochloric acid is used to test for the presence of this mineral in rocks. The acid fizzes by producing carbon dioxide when dripped onto a mineral made of calcium carbonate.

$$Ca^{2+}CO_3^{2-}(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq) + CO_2(g) + H_2O(l)$$

In this case, the Ca^{2+} and $2Cl^-$ are spectator ions, so the ionic equation is:

$$CO_3^{2-}(s) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$$

Test yourself

2 Give the names and symbols of the ions formed when these acids dissolve in water:

- **a)** nitric acid, HNO_3
- **b)** sulfuric acid, H_2SO_4.

3 Write full balanced equations for the reactions of:

- **a)** zinc with sulfuric acid
- **b)** calcium oxide with nitric acid
- **c)** sodium carbonate with hydrochloric acid.

4 Rewrite the equations in Question 3 as ionic equations.

Key term

An **ionic precipitation reaction** is a reaction which produces a solid precipitate on mixing two solutions containing ions.

Ionic precipitation reactions

The simplest examples of **ionic precipitation reactions** involve mixing two solutions of soluble ionic compounds. The positive ions from one compound combine with the negative ions of the other to form an insoluble precipitate.

When ionic compounds dissolve in water, the ions move away from the crystals and each ion becomes surrounded by water molecules. So a solution of potassium iodide, KI, in water, for example, contains separate $K^+(aq)$ ions and $I^-(aq)$ ions mixed up with water molecules.

On mixing solutions of potassium iodide and lead(II) nitrate, there are two possible new combinations of ions: lead ions with iodide ions, and potassium ions with nitrate ions. Lead(II) iodide is insoluble, so it precipitates (Figure 4.3). Potassium nitrate is soluble so the potassium and nitrate ions stay in solution.

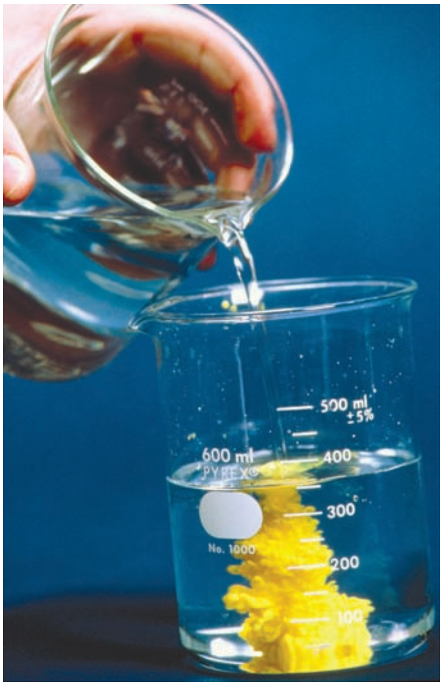


Figure 4.3 A precipitate of lead(II) iodide forms on adding a solution of potassium iodide to a solution of lead(II) nitrate.

$$Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$$

Rewriting the equation in terms of aqueous ions, gives:

$$Pb^{2+}(aq) + \underbrace{2NO_3^-(aq) + 2K^+(aq)}_{\text{spectator ions}} + 2I^-(aq) \rightarrow PbI_2(s) + \underbrace{2K^+(aq) + 2NO_3^-(aq)}_{\text{spectator ions}}$$

Cancelling the spectator ions, leads to the simpler, ionic equation for the reaction.

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

The solubility rules in Table 4.1 can be used to predict whether or not a precipitate forms on mixing two solutions.

Table 4.1 Solubilities of acids, bases and salts.

Type of compound	Soluble in water	Insoluble in water
Acids	All common acids	
Metal hydroxides and carbonates	Soluble hydroxides and carbonates are alkalis. They include the hydroxides of sodium and potassium, and also the carbonates of sodium and potassium. Calcium hydroxide is slightly soluble.	All other metal oxides and hydroxides. All other carbonates.
Salts	All nitrates.	
	All chlorides…	… except silver chloride and lead chloride.
	All sulfates … (Calcium sulfate and silver sulfate are slightly soluble.)	… except barium sulfate and lead sulfate.
	All sodium, potassium and ammonium salts.	

Test yourself

5 Use Table 4.1 to decide whether or not a precipitate forms on mixing solutions of these pairs of substances. If yes, state the name and formula of the precipitate and give the ionic equation for the reaction.

- **a)** zinc sulfate and barium nitrate
- **b)** potassium nitrate and copper(II) sulfate
- **c)** sodium carbonate and calcium chloride
- **d)** lead(II) nitrate and sodium chloride
- **e)** sodium hydroxide and copper(II) sulfate

6 Classify these reactions as redox, acid–alkali, precipitation or thermal decomposition:

- **a)** $CaCl_2(aq) + K_2SO_4(aq) \rightarrow CaSO_4(s) + 2KCl(aq)$
- **b)** $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
- **c)** $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$
- **d)** $Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$

4.2 Group 1, the alkali metals

Inorganic chemistry is the study of the hundred or so elements and their compounds. The amount of information can be bewildering, hence the importance of the periodic table which helps to identify patterns in all the facts about properties and reactions.

The Group 1 elements are better known as the alkali metals. These elements are more alike than the elements in any other group. Their compounds are widely used as chemical reagents.

The elements

The metals are soft and easily cut with a knife. They are shiny when freshly cut but quickly become dull in air as they react with moisture and oxygen (Figures 4.4, 4.5 and 4.6). Laboratory specimens are kept in oil to protect them from the air.

Tip

The detailed study of Group 1 chemistry is not required for examinations. However, there are Group 1 compounds that you need to know about because they are important chemical reagents. You also have to know the results of flame tests for some Group 1 compounds. You are expected to be able to compare some properties of the carbonates and nitrates of Group 2 elements with those of Group 1 elements.

Figure 4.4 A sample of lithium metal. Lithium compounds such as lithium carbonate are used in drugs for treating mental illness. Other lithium compounds are important reagents for organic synthesis.

Figure 4.5 A sample of sodium metal. Sodium metal is a powerful reducing agent used to extract titanium and some other metals. Sodium vapour is used in street lights. Sodium hydroxide is the most important industrial alkali. Many other sodium compounds are important commercially.

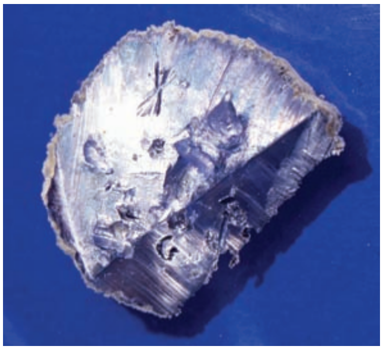


Figure 4.6 A sample of potassium metal. Potassium ions are an essential nutrient for plants and an ingredient of NPK fertilisers. There are many other important potassium compounds.

Key term

A **trend** describes the way in which a property increases or decreases along a series of elements or compounds. In the periodic table the term can describe the variations of a property down a group or across a period.

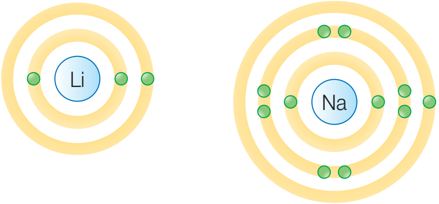


Figure 4.7 Diagrams to represent the electron configurations of lithium and sodium.

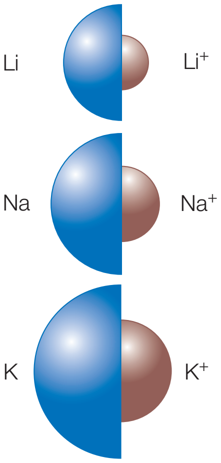


Figure 4.8 Relative sizes of the atoms and ions of Group 1 elements.

Atoms of the elements

The Group 1 elements have similar chemical properties because their atoms have similar electron structures with one electron in the outer s orbital (Figure 4.7 and Section 1.7). Even so, there are **trends** in properties down the group from lithium to caesium.

The atoms change down the group: the charge on the nucleus increases; also the number of filled inner shells increases and so the atomic radius increases. The number of electrons in the inner shells is always one less than the number of protons in the nucleus. So the shielding effect of the inner electrons means that the effective nuclear charge attracting the outer electron is 1+. Down the group, the outer electrons get further and further away from the same effective nuclear charge and so they are held less strongly (Figure 4.8 and Section 1.8).

Test yourself

7 The electron configuration of lithium can be shortened to $[He]2s^1$. Using this style, give the electron configurations of:

a) sodium

b) potassium.

8 The first ionisation energies of the alkali metals get smaller down the group. Why is this?

9 Explain why the ions of Group 1 metals are smaller than their atoms.

Oxidation states

When the atoms of alkali metals react, they lose their single s electron from the outer shell, turning into ions with a single positive charge: Li^+, Na^+, K^+ and so on. So the only oxidation state of these elements in their compounds is +1.

Reactions of the elements

The alkali metals are powerful reducing agents because they react by giving up electrons to form M^+ ions.

All the metals react with water to form hydroxides, MOH, and hydrogen (where M is Li, Na, K and so on). The rate and violence of the reaction increases down the group. Lithium reacts steadily with cold water giving off a steady stream of bubbles of hydrogen. Sodium melts to form a shiny bead which skates around on the surface of the water. The reaction with potassium is so violent that the hydrogen catches fire and burns with a violet flame as the metal rapidly reacts.

$$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$$

All the metals react vigorously with chlorine to form colourless, ionic chlorides, M^+Cl^-. The chlorides are soluble in water, forming colourless solutions.

$$2K(s) + Cl_2(g) \rightarrow 2KCl(s)$$

Test yourself

10 Write balanced equations and use oxidation numbers to show that sodium acts as a reducing agent when it reacts with:

a) water

b) chlorine.

Key term

Bases are 'anti-acids' – they are the chemical opposites of acids. Acids donate (give up) hydrogen ions; bases (such as the oxide ion, hydroxide ion and carbonate ion) accept hydrogen ions.

Tip

It is the hydroxide ion which is the base and which makes the solutions alkaline, not the metal ions.

4.3 Properties of the compounds of Group 1 metals

The hydroxides

The hydroxides are all white solids, commonly supplied as pellets or flakes (Figure 4.9). These are soluble in water, forming alkaline solutions, although the solubility of these hydroxides increases down the group. The hydroxides are strong **bases** because they are fully ionised in water, giving solutions containing hydroxide ions.

AnalaR
Sodium hydroxide
NaOH=40.00
CAUTION
Corrosive
BDH Chemicals

Figure 4.9 Sodium hydroxide, NaOH, is deliquescent, which means that it picks up water from moist air and then dissolves in it. Sodium hydroxide is a strong base – it dissolves in water to form a highly alkaline solution. The traditional name for the alkali is 'caustic soda'. Sodium hydroxide is highly corrosive and more hazardous to the skin and eyes than many acids.

The carbonates

The carbonates are all white with the general formula M_2CO_3. They are unusual metal carbonates in that they dissolve in water. Solutions of these carbonates are alkaline because the carbonate ions remove H^+ ions from water molecules to form hydrogen carbonate ions and hydroxide ions. It is the hydroxide ions that make the solution alkaline.

$$CO_3^{2-}(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + OH^-(aq)$$

Another unusual feature of Group 1 carbonates is that most of them do not decompose on heating. The exception is lithium carbonate, which breaks down to the oxide and carbon dioxide when hot (see Section 4.7).

Test yourself

11 Write full and ionic equations for the reaction of:
- **a)** potassium hydroxide with dilute sulfuric acid
- **b)** aqueous sodium carbonate with dilute nitric acid.

12 Write balanced equations for the thermal decomposition of:
- **a)** lithium carbonate
- **b)** lithium nitrate.

The nitrates

The nitrates of Group 1 metals are white crystalline solids with the formula MNO_3. They are very soluble in water.

The crystals of sodium and potassium nitrates are much harder to decompose on heating than most other metal nitrates. On heating, these nitrates first melt and then on stronger heating start to decompose, giving off oxygen. They only decompose as far as the nitrite.

$$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$$

Lithium nitrate is the exception. It behaves like most other metal nitrates, decomposing to the oxide, nitrogen dioxide and oxygen (see Section 4.7).

Sodium and potassium compounds as chemical reagents

The compounds of sodium and potassium are widely used as chemical reagents. One reason for this is that the ions of alkali metals are unreactive. So they act as spectator ions which take no part in reactions when the reagents are used.

A second reason is that most sodium and potassium compounds are soluble in water, including their hydroxides and carbonates. Most other metal hydroxides and carbonates are insoluble so not available in aqueous solution.

A third reason is that the ions of alkali metals are colourless in aqueous solution so they do not hide or interfere with colour changes. Sodium or potassium compounds are coloured only if the negative ion is coloured. Potassium chromate(VI), for example, is yellow because CrO_4^{2-} ions are yellow.

Flame colours

Flame colours help to detect some metal ions (Figures 4.10 and 4.11, and Table 4.2). They are particularly useful in identifying Group 1 metal ions, which are otherwise very similar.

Ionic compounds such as sodium chloride do not burn during a flame test. The energy from the flame excites the outer electrons of sodium ions, raising them to higher energy levels. The atoms then emit the characteristic yellow light as the electrons drop back to lower energy levels (Section 1.5).

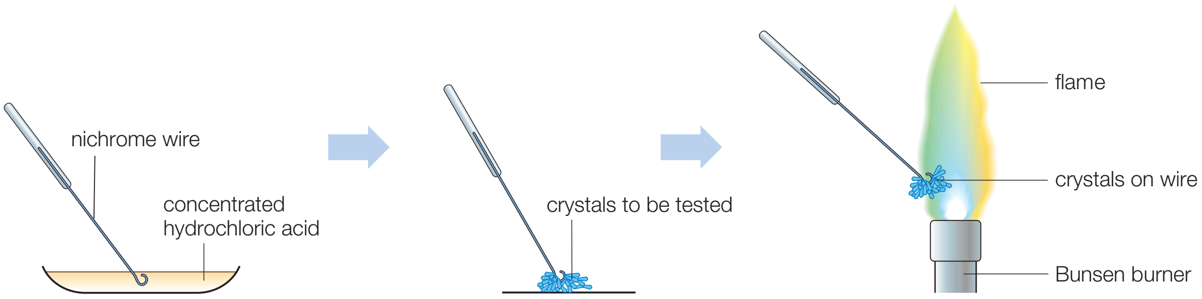


Figure 4.10 Procedure for a flame test. Chlorides evaporate more easily and so colour flames more strongly than less volatile compounds. Concentrated hydrochloric acid converts involatile compounds such as carbonates to chlorides.

Table 4.2 Flame colours of Group 1 metal compounds.

Metal ion	Colour
Lithium	Bright red
Sodium	Bright yellow
Potassium	Lilac

Tip

Some chemical reagents contain traces of sodium compounds as impurities. The sodium flame colour is so strong that it can easily obscure the colour of other flames, especially the pale lilac flame from potassium compounds.

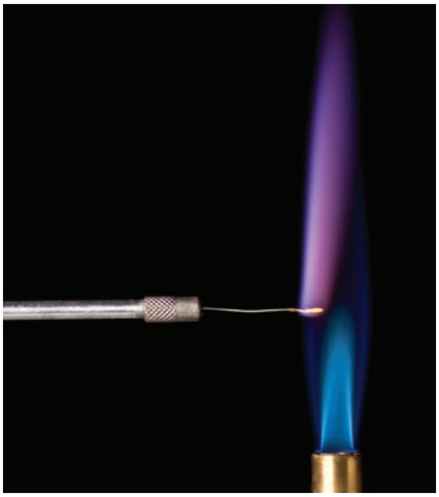


Figure 4.11 The flame colour from a potassium salt.

Test yourself

13 Classify these reactions of Group 1 elements and compounds as acid–base, thermal decomposition or redox.

a) $2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$

b) $2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$

c) $2Li(s) + Br_2(l) \rightarrow 2LiBr(s)$

d) $Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$

Figure 4.12 Stalactites and stalagmites in a limestone cave. Stalactites are formed by calcium carbonate, dissolved in ground water, dripping through into caves. The calcium carbonate then precipitates out of the water, forming rock. Stalagmites are formed when the water falls from the stalactite onto the cave floor.

4.4 Group 2, the alkaline earth metals

Group 2 elements belong to the family of alkaline earth metals. Many of the compounds of these elements occur as minerals in rocks – hence the name ‘earth metals’. Chalk, marble and limestone, for example, are forms of calcium carbonate (Figure 4.12). Dolomite consists of a mixture of calcium and magnesium carbonates. Fluorspar is a form of calcium fluoride which is mined as the ornamental mineral (Figure 4.13). These Group 2 compounds are insoluble, unlike the equivalent Group 1 compounds. They do not dissolve in water.

The elements

The Group 2 metals are harder and denser than Group 1 metals and they have higher melting temperatures (Figure 4.14). In air, the surface of the metals is covered with a layer of oxide.

Figure 4.13 A sample of fluorite mined in Weardale, County Durham.

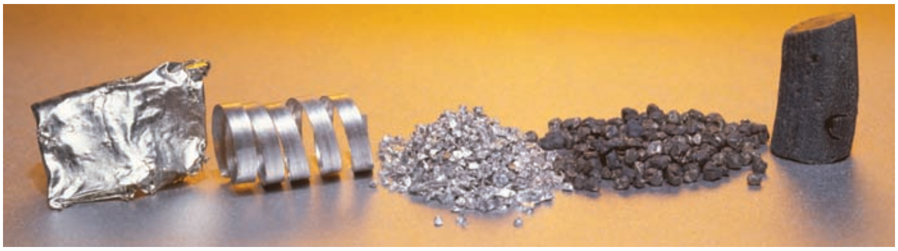


Figure 4.14 Samples of the Group 2 metals. From the left: beryllium, magnesium, calcium, strontium and barium.

Table 4.3 The shortened forms of the electron configurations of Group 2 metals.

Metal	Electron configuration
Beryllium, Be	[He]$2s^2$
Magnesium, Mg	[Ne]$3s^2$
Calcium, Ca	[Ar]$4s^2$
Strontium, Sr	[Kr]$5s^2$
Barium, Ba	[Xe]$6s^2$

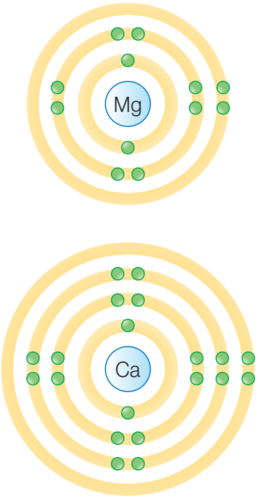


Figure 4.15 Diagrams to represent the electron configurations of magnesium and calcium atoms.

The first member of the group, beryllium (Be), is a strong metal with a high melting temperature, but its density is much less than that of transition metals such as iron. The element makes useful alloys with other metals.

Magnesium is manufactured by the electrolysis of molten magnesium chloride from sea water or from salt deposits. The low density of the metal helps to make light alloys, especially with aluminium. These alloys, which are strong for their weight, are especially useful for car and aircraft manufacture.

Barium is a soft, silvery-white metal. It is so reactive with air and moisture that it is generally stored under oil, like the alkali metals.

Atoms and ions

Like the atoms of the alkali metals, the Group 2 atoms change down the group: the charge on the nucleus increases, and the number of filled inner shells also increases (Table 4.3 and Figure 4.15).

The increasing number of filled inner shells means that atomic and ionic radii increase down the group (Figure 4.16). For each element, the 2+ ion is smaller than the atom because of the loss of the outer shell of electrons. The tendency to react and form ions increases down the group.

The first and second ionisation energies decrease down the group (Figure 4.17). The shielding effect of the inner electrons means that the effective nuclear charge attracting the outer electron is 2+. Down the group the outer s electrons get further and further away from the same effective nuclear charge, and so they are held less strongly and the ionisation energies decrease. This trend helps to account for the increasing reactivity of the elements down the group.

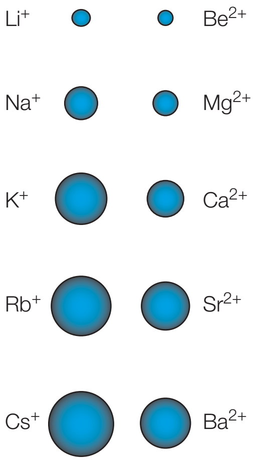


Figure 4.16 Comparison of the trend in ionic radii of Group 1 and Group 2 metals.

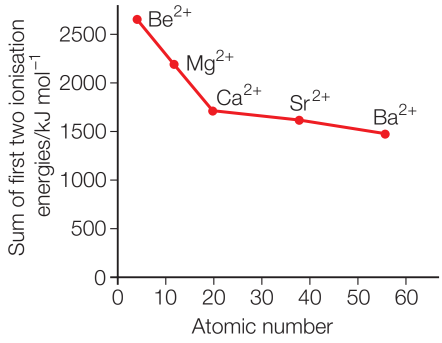


Figure 4.17 Graph showing the trend in the sum of the first two ionisation energies of Group 2 metals: $M(g) \longrightarrow M^{2+}(g) + 2e^-$.

The removal of a third electron to form a 3+ ion takes much more energy because the third electron has to be removed against the attraction of a much larger effective nuclear charge. This means that it is never energetically favourable for the metals to form M^{3+} ions.

Test yourself

14 Write the full electron configurations of the atoms and ions of Mg, Ca and Sr showing the numbers of s, p and d electrons (Section 1.6).

15 Explain why Group 2 ions in any period are smaller than the Group 1 ions in that period.

16 Explain why the radii of Group 2 metal ions increase down the group.

Tip

Always check carefully that you are using the right term when answering questions about the radii of atoms and ions. Be sure to distinguish atomic radii from ionic radii.

Oxidation states

All the Group 2 metals have similar chemical properties because they have similar electron structures with two electrons in an outer s orbital. When the metal atoms react to form ions, they lose the two outer electrons, giving ions with a 2+ charge: Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. So these elements exist in the +2 oxidation state in all their compounds.

4.5 Reactions of the Group 2 elements

Group 2 metals are reducing agents. Apart from beryllium, they readily give up their two s electrons to form M^{2+} ions (where M represents Mg, Ca, Sr or Ba).

$$M \rightarrow M^{2+} + 2e^-$$

Tip

Note that beryllium is not a typical Group 2 element and so the coverage of its chemical properties in this chapter is limited. The small size of the beryllium ion (electron configuration $1s^2$) means that it has a much higher polarising power than other Group 2 ions (Section 4.7). The polarising power of the ions of a metal determine to a large extent the type of bonding between the element and non-metals such as oxygen and chlorine and hence the chemical characteristics of the compounds.

Reactions with oxygen

Apart from beryllium, the Group 2 metals burn in oxygen on heating to form white, ionic oxides, consisting of M^{2+} ions and O^{2-} ions.

Magnesium burns very brightly in air with an intense white flame and for this reason, magnesium powder is used in fireworks and flares. The reaction produces the white solid magnesium oxide, MgO (Section 3.2).

Calcium also burns brightly in air but with a red flame forming the white solid calcium oxide, CaO. Strontium reacts in a similar way.

Barium burns in excess air or oxygen with a green flame to form a peroxide, BaO_2, which contains the peroxide ion, $O_2{}^{2-}$.

Reactions with water

The metals Mg to Ba in Group 2 react with water. The reactions are not as vigorous as the reactions of the Group 1 metals, but, as in Group 1, the rate of reaction increases down the group.

Magnesium reacts very slowly with cold water producing the hydroxide, $Mg(OH)_2$, and hydrogen. This metal reacts much more rapidly on heating in steam.

$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$$

Calcium reacts with cold water to produce hydrogen calcium hydroxide. Initially the $Ca(OH)_2$ formed dissolves, but the solubility is low so that, as more is formed, the solution soon becomes saturated and a white precipitate appears.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$

Barium reacts even faster with cold water and its hydroxide is more soluble.

Reactions with chlorine

All the metals, including beryllium, react with chlorine on heating to form white chlorides, MCl_2.

$$Be(s) + Cl_2(g) \rightarrow BeCl_2(s)$$

Test yourself

17 What is the oxidation state of oxygen in barium peroxide?

18 Write balanced equations for the reactions of:

- **a)** strontium with oxygen
- **b)** barium with oxygen
- **c)** strontium with chlorine
- **d)** barium with water.

4.6 Properties of the compounds of Group 2 metals

Key term

A **basic oxide** is a metal oxide which reacts with acids to form salts and water. It is the oxide ion which acts as a base by taking a hydrogen ion from the acid. Basic oxides which dissolve in water are alkalis.

The oxides

Apart from beryllium oxide, the oxides of Group 2 metals are **basic oxides**. They react with acids to form salts.

$$CaO(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l)$$

Magnesium oxide is a white solid. In water it turns to magnesium hydroxide, which is slightly soluble. Magnesium oxide has a high melting temperature and is used as a heat-resistant ceramic to line furnaces.

Calcium oxide is a white solid made by heating calcium carbonate. Calcium oxide reacts very vigorously with cold water, hence its traditional name 'quicklime'. The product is calcium hydroxide.

The hydroxides

The hydroxides of the elements Mg to Ba are:

- similar in that they all have the formula $M(OH)_2$ and are, to some degree, soluble in water forming alkaline solutions
- different in that their solubility increases down the group.

Magnesium hydroxide is the active ingredient in milk of magnesia, used as an antacid and laxative. It is insoluble in water.

Calcium hydroxide is slightly soluble in water forming an alkaline solution, usually called limewater. The limewater test for carbon dioxide works because a solution of calcium hydroxide reacts with the gas forming a white, insoluble precipitate of calcium carbonate.

Barium hydroxide is the most soluble of the hydroxides. It is sometimes used as an alkali in chemical analysis. It has the advantage over sodium and potassium hydroxides in that it cannot be contaminated by its carbonate because barium carbonate is insoluble in water.

Test yourself

19 Write balanced equations for the reactions:

a) magnesium oxide with dilute hydrochloric acid

b) calcium oxide with water

c) limewater with carbon dioxide.

Tip

There is no simple explanation for the trends in solubility of alkaline earth metal compounds down the group. If the negative ion is small (as in the oxide and hydroxide), then the compounds of the metal with the smallest ions, Mg^{2+}, are least soluble. If the negative ion is relatively large (as in the sulfates and carbonates), then the metal compounds of the metal with the largest ions, Ba^{2+}, are least soluble. In other words, the rule of thumb is that these compounds tend to be insoluble if both ions are small, or both ions are big.

The carbonates

The carbonates of Group 2 metals (Mg to Ba) are:

- similar in that they all have the formula MCO_3, are insoluble in water, react with dilute acids and decompose on heating to give the oxide and carbon dioxide

  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

- different in that they become more difficult to decompose down the group – in other words, they become more thermally stable (Section 4.7).

The nitrates

The nitrates of Group 2 metals (Mg to Ba) are:

- similar in that they all have the formula $M(NO_3)_2$, are colourless crystalline solids, are very soluble in water and decompose to the oxide on heating

  $2Mg(NO_3)_2(s) \rightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$

- different in that they become more difficult to decompose down the group (Section 4.7).

The sulfates

The sulfates are:

- similar in that they are all colourless solids with the formula MSO_4
- different in that they become less soluble down the group.

Epsom salts consist of hydrated magnesium sulfate, $MgSO_4.7H_2O$, which is a laxative.

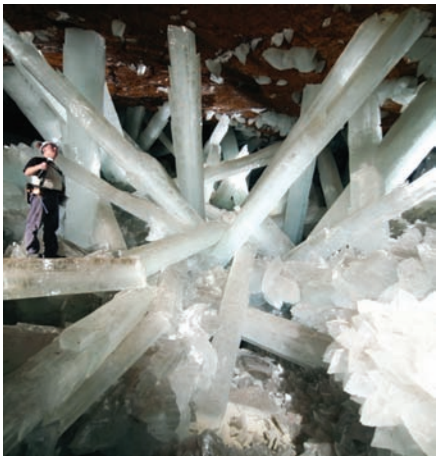


Figure 4.18 A geologist in the Cave of Crystals (Cueva de los Cristales) in Naica Mine, Chihuahua, Mexico. The crystals are the largest known in the world, and are formed of the selenite form of gypsum (hydrated calcium sulfate).

A hydrated form of calcium sulfate occurs naturally as gypsum (Figure 4.18) which is produced on a large scale by the process that removes sulfur dioxide from the flue gases of coal-fired power stations. Plaster of Paris is the main ingredient of building plasters and much is used to make plasterboard. The white powder is made by heating gypsum in kilns to remove most of the water of crystallisation. Stirring plaster of Paris with water produces a paste which soon sets as it turns back into interlocking grains of gypsum. Plaster makes good moulds because it expands slightly as it sets so that it fills every crevice.

Barium occurs naturally in minerals such as witherite, $BaCO_3$ and as baryte, $BaSO_4$ (Figure 4.19). Barium sulfate absorbs X-rays strongly so it is the main ingredient of 'barium meals' used to diagnose disorders of the stomach or intestines. Soluble barium compounds are toxic but barium sulfate is very insoluble so it is not absorbed into the bloodstream from the gut. X-rays cannot pass through the 'barium meal', which therefore creates a shadow on the X-ray film (Figure 4.20).

Tip

Magnesium compounds do not give a colour when heated in a flame. The flame test colour for magnesium compounds is *not* 'bright white'.

Figure 4.19 Sample of baryte (barium sulfate) from Poland.

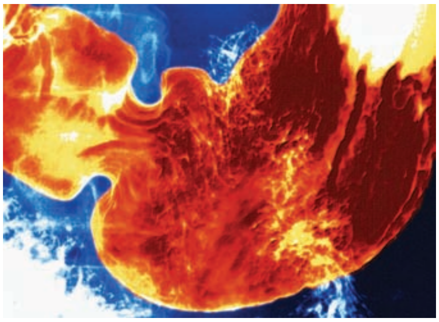


Figure 4.20 Coloured X-ray photograph of the healthy stomach of a patient who has taken a barium meal.

A soluble barium salt can be used to test for sulfate ions because barium sulfate is insoluble, even when the solution is acidic. Adding a solution of barium nitrate or barium chloride to an acidified solution produces a white precipitate only if sulfate ions are present.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow \underset{\text{white precipitate}}{BaSO_4(s)}$$

Table 4.4 Flame colours of Group 2 metal compounds.

Metal ion	Colour
Beryllium	No colour
Magnesium	No colour
Calcium	Brick red
Strontium	Bright red
Barium	Pale green

Flame colours

Flame tests help to identify compounds of calcium, strontium and barium (Table 4.4).

4.7 Thermal stability of the carbonates and nitrates

Whenever chemists use the term 'stability' they are making comparisons. For the Group 2 carbonates, the question is which is more stable – the metal carbonate, or a mixture of the metal oxide and carbon dioxide?

The carbonates and nitrates of Group 1 and 2 elements are ionic. Chemists explain differences in the **thermal stabilities** of their carbonates and nitrates in terms of two factors:

- the charge on the metal ions
- the size of the metal ions.

Key term

Thermal stability is an indication of the ease with which compounds decompose on heating. Compounds are stable if they do not tend to decompose into their elements or into other compounds. A compound which is stable at room temperature and pressure may become more or less stable as conditions change.

Group 2 carbonates and nitrates are generally less stable than the corresponding Group 1 compounds. This suggests that the larger the charge on the metal ion and the smaller the metal ion, the less stable the compounds.

The carbonates become more stable down both Group 1 and Group 2. This helps to confirm that, the larger the metal ion, the more stable the compounds.

Beryllium carbonate is so unstable that it does not exist. Table 4.5 shows the temperatures at which the carbonates of Group 2 metals begin to decompose. The values indicate that magnesium carbonate is the least stable. It decomposes easily to the oxide and carbon dioxide when heated with a Bunsen flame. Barium carbonate is the most stable.

Table 4.5 The temperature at which Group 2 carbonates begin to decompose.

Carbonate	Decomposition temperature/°C
$MgCO_3$	540
$CaCO_3$	900
$SrCO_3$	1280
$BaCO_3$	1360

Trends in the thermal stability of carbonates and nitrates can be explained in terms of the **polarising power** of the metal ions. The larger the charge on an ion and the smaller its radius, the greater its charge density. The greater the charge density, the greater the polarising power of the ion. A metal ion with a higher polarising power attracts the bonding electrons in neighbouring ions more strongly. This pull on the electrons of an ion, such as a carbonate ion, distorts the bonding and makes it easier to break up the negative ion into an oxide ion and carbon dioxide (Figure 4.21).

Key term

Polarising power gives an indication of the extent to which a positive ion is able to distort the electron cloud around a neighbouring negative ion. The larger the charge on a positive ion and the smaller its size, the greater its polarising power.

Down Group 2, for example, the charge on the metal ion is always 2+. However the increasing number of full, inner shells means that the ionic radii increase down the group. As a result, the charge density of the ions decreases down the group. So the trend in polarising power is $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. This means that the thermal stability of carbonates and nitrates increases down the group.

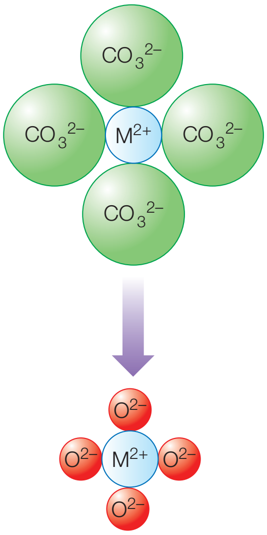


Figure 4.21 Decomposition of a Group 2 carbonate to a Group 2 oxide. The smaller the metal ion, the less stable the carbonate.

Test yourself

20 a) Draw and label a diagram of a simple apparatus to investigate the trend in the thermal stability of Group 2 carbonates.

b) Describe the observations you would expect to make with the carbonates of magnesium, calcium and barium.

21 Write equations for:

a) the thermal decomposition of magnesium carbonate

b) the reaction of magnesium carbonate with hydrochloric acid

c) the thermal decomposition of calcium nitrate

d) the reaction of barium nitrate solution with zinc sulfate solution.

22 With the help of oxidation numbers, identify the elements that are oxidised and reduced during the thermal decomposition of magnesium nitrate.

23 Why does calcium carbonate decompose on heating strongly in a Bunsen flame while potassium carbonate does not?

4.8 Group 7, the halogens

Fluorine, chlorine, bromine and iodine belong to the family of halogens. All four are reactive non-metals – fluorine and chlorine extremely so. The elements are hazardous because they are so reactive. For the same reason, they are never found free in nature. However, they do occur as compounds with metals. Many of the compounds of Group 7 elements are salts – hence the name 'halo-gen' meaning 'salt-former'. Halogen compounds are important economically as the ingredients of plastics, pharmaceuticals, anaesthetics and dyestuffs.

The elements

Under laboratory conditions chlorine is a yellow-green gas (Figure 4.22), bromine is a dark red liquid (Figure 4.23), while iodine is a dark grey solid (Figure 4.24).

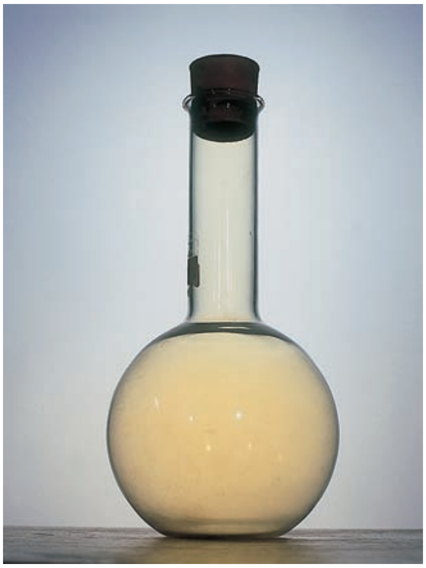


Figure 4.22 Chlorine gas.

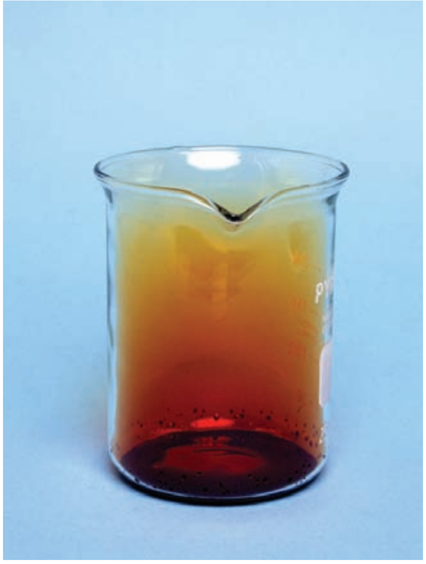


Figure 4.23 Bromine is a dark red liquid at room temperature. It is very volatile, giving off a choking, orange vapour. For this reason, it should always be studied in a fume cupboard.

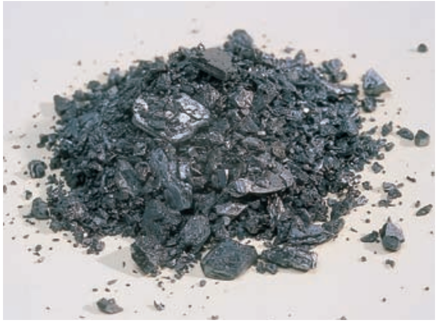


Figure 4.24 Iodine is a lustrous grey-black solid at room temperature. It sublimes when gently warmed to give a purple vapour.

Fluorine is much too dangerous to be used in normal laboratories. Astatine, the final member of the group is the rarest naturally occurring element. It is highly radioactive – its most stable isotope has a half-life of just over 8 hours.

All the halogens consist of diatomic molecules, X_2, linked by a single covalent bond. They are all volatile. Intermolecular forces (London forces) increase down the group as the numbers of electrons in the molecules increase (Section 2.6). The larger molecules are more polarisable than the smaller molecules, so melting temperatures and boiling temperatures rise down the group.

The halogens have similar chemical properties because they all have seven electrons in the outer shell – one fewer than the next noble gas in Group 8 (Table 4.6).

Fluorine is the most electronegative of all elements. Its oxidation state is −1 in all its compounds. Uses of fluorine include the manufacture of a wide range of compounds consisting of only carbon and fluorine (fluorocarbons). The most familiar of these is the very slippery, non-stick polymer, poly(tetrafluorethene).

Table 4.6 Shortened form of the electron configurations of the halogens.

Halogen	Electron configuration
Fluorine, F	[He]$2s^2 2p^5$
Chlorine, Cl	[Ne]$3s^2 3p^5$
Bromine, Br	[Ar]$3d^{10} 4s^2 4p^5$
Iodine, I	[Kr]$4d^{10} 5s^2 5p^5$

Chlorine reacts directly with most elements. In its compounds, chlorine is usually present in the −1 oxidation state, but it can be oxidised to positive oxidation states by oxygen and fluorine. Most chlorine is used in the production of polymers such as PVC. Water companies use chlorine to kill bacteria in drinking water, while another important use of the element is to bleach paper and textiles.

Bromine, like the other halogens, is a reactive element but it is a less powerful oxidising agent than chlorine. Bromine is used to make a range of products including flame retardants, medicines and dyes.

Iodine is also an oxidising agent but it is less powerful than bromine. Iodine and its compounds are used to make many products including medicines, dyes and catalysts. In many regions, sodium iodide is added to table salt to supplement iodine in the diet and to drinking water to prevent goitre – a swelling of the thyroid gland in the neck. Iodine is needed in our diet so that the thyroid gland can make the hormone thyroxine, which regulates growth and metabolism.

Test yourself

24 Predict the state of the following at room temperature and pressure, giving your reasons:

a) fluorine **b)** astatine.

25 Write down the full electron configurations of:

a) a chlorine atom **b)** a chloride ion

c) a bromine atom **d)** a bromide ion.

26 Explain why:

a) the atomic radii of halogen atoms increase down the group

b) the ionic radii of halides are larger than their corresponding atomic radii.

27 Draw dot-and-cross diagrams, showing just the electrons in the outer shells of the atom, to describe the bonding in:

a) a fluorine molecule

b) a molecule of hydrogen bromide

c) a molecule of iodine monochloride, ICl.

Tip

In exams it is important to avoid losing marks by careless use of chemical language. For example, you must distinguish the element ‘chlorine’ from the ‘chloride’ ion in its compounds.

Solutions of the halogens

The halogens dissolve freely in hydrocarbon solvents, such as cyclohexane. When dissolved in cyclohexane, the solutions have a very similar colour to the free halogen vapours. So iodine in cyclohexane, for example, has an attractive violet colour (Figure 4.25).

The halogens are less soluble in water than in organic solvents. Aqueous chlorine and bromine are useful reagents. Their colours are similar to the colours of their vapours. These elements also react with water (Section 4.11).

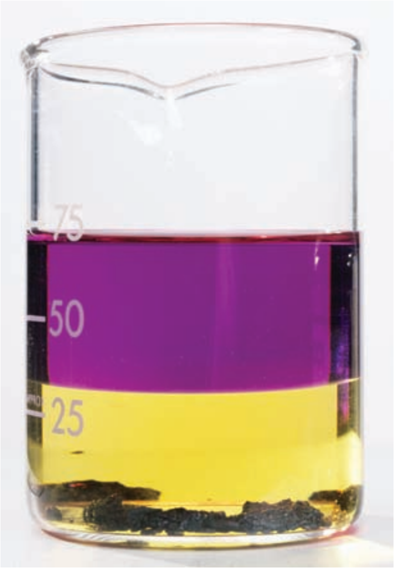


Figure 4.25 Iodine dissolved in water (bottom layer). There is some solid iodine at the bottom of the beaker. Iodine does not dissolve well in water, so the brown colour of the solution is faint. Iodine does dissolve well in cyclohexane, giving a strong purple colour.

Iodine does not dissolve in water, but it does dissolve in aqueous potassium iodide. Iodine dissolves in this way because iodine molecules react with iodide ions to form triiodide ions, I_3^-.

$$I_2(s) + I^-(aq) \rightarrow I_3^-(aq)$$

A reagent labelled 'iodine solution' is normally $I_2(s)$ in KI(aq). The $I_3^-(aq)$ ion is a yellow-brown colour which explains why aqueous iodine looks quite different from a solution of iodine in a non-polar solvent such as cyclohexane. The aqueous solution is yellow when very dilute but dark orange-brown when more concentrated.

Test yourself

28 Why are the halogens more soluble in cyclohexane than in water?

4.9 Reactions of the Group 7 elements

The halogens are all oxidising agents. The reactions of the halogens show a clear trend in their reactivity as oxidising agents down the group. Fluorine is the most powerful oxidising agent and iodine the least powerful.

Halogen atoms are highly electronegative (Section 2.5), although the electronegativity decreases down the group. They form ionic compounds or compounds with polar bonding.

Reactions of halogens with metals

Chlorine and bromine react with s-block metals to form ionic halides in which the halogen atoms gain one electron to fill the outermost p sub-shell.

Iodine also reacts with metals to form iodides, but because of the polarisability of the large iodide ion, those iodides formed with small cations such as Li^+, or highly charged cations such as Al^{3+}, are essentially covalent (Section 2.5). The halogens also react with most metals in the d block. Hot iron, for example, burns brightly in chlorine, forming iron(III) chloride (Figure 4.26). The reaction with bromine is similar but much less exothermic. Iron(III) iodide does not exist because iodide ions reduce iron(III) ions to iron(II) ions. So, heating iron with iodine vapour produces iron(II) iodide.

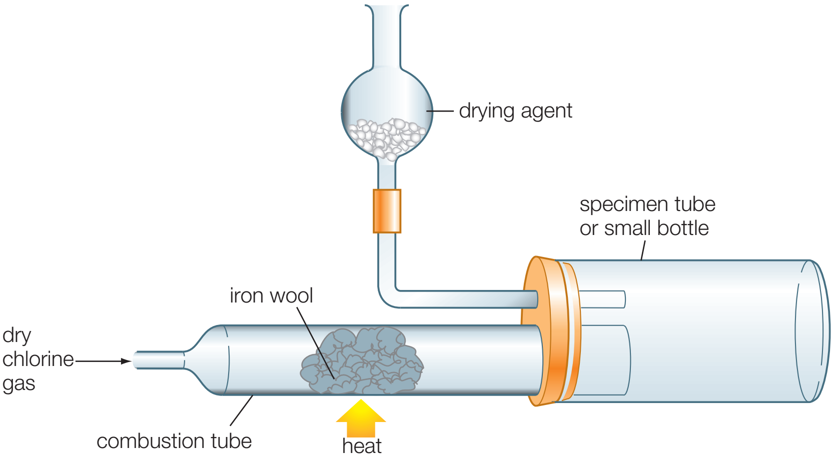


Figure 4.26 The laboratory apparatus for making anhydrous iron(III) chloride. This reaction must be carried out in a fume cupboard.

Test yourself

29 Write balanced equations for these reactions, and show the changes in oxidation states:

- **a)** bromine with magnesium
- **b)** chlorine with iron
- **c)** iodine with iron.

30 In Figure 4.26, explain the reasons for:

- **a)** carrying out the reaction in a fume cupboard
- **b)** drying the chlorine gas
- **c)** using iron wool instead of small lumps of iron
- **d)** collecting the product in a specimen tube
- **e)** allowing excess gas to escape through a tube with a drying agent.

Reactions of halogens with non-metals

Chlorine reacts with most non-metals to form molecular chlorides. Hot silicon, for example, reacts to form silicon tetrachloride, $SiCl_4(l)$, and phosphorus produces phosphorus trichloride, $PCl_3(l)$ or phosphorus pentachloride, $PCl_5(s)$, depending on whether the supply of the gas is limited or in excess. However, chlorine does not react directly with carbon, oxygen or nitrogen.

Hydrogen burns in chlorine to produce the colourless, acidic gas hydrogen chloride, HCl. Igniting a mixture of chlorine and hydrogen gases leads to a violent explosion.

Bromine also oxidises non-metals such as sulfur and hydrogen on heating, forming molecular bromides. A mixture of bromine vapour and hydrogen gas reacts smoothly with a pale bluish flame.

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$

Iodine oxidises hydrogen on heating to form hydrogen iodide. Unlike the reactions of chlorine and bromine, this is a reversible reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Tip

Be careful to distinguish hydrogen chloride gas, HCl(g) from hydrochloric acid, HCl(aq). Hydrochloric acid is a solution of hydrogen chloride in water. Even concentrated hydrochloric acid is a solution.

Reactions of halogens with aqueous Fe^{2+} ions

Chlorine and bromine can oxidise iron(II) ions in solution to iron(III) ions. Iodine is such a weak oxidising agent that it cannot oxidise iron(II) compounds.

$$2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$$

Test yourself

31 Show that the reactions of chlorine, bromine and iodine with hydrogen illustrate a trend in reactivity down Group 7.

32 Predict the formula of the product and vigour of the reaction when fluorine reacts with hydrogen.

33 Explain, in terms of structure and bonding, why silicon tetrachloride is a liquid.

34 Write equations for the reactions and use oxidation numbers to show that:

- **a)** phosphorus is oxidised when it reacts with chlorine
- **b)** chlorine is reduced when it displaces iodine from a solution of potassium iodide.

35 Write ionic half-equations and the overall ionic equation for the reaction of bromine with aqueous iron(II) ions.

4.10 Halogens in oxidation state –1

Halide ions

Halide ions are the ions of the halogen elements in oxidation state −1. They include the fluoride (F^-), chloride (Cl^-), bromide (Br^-) and iodide (I^-) ions.

Tip

Remember that halide ions are colourless. It is the halogen molecules that are coloured.

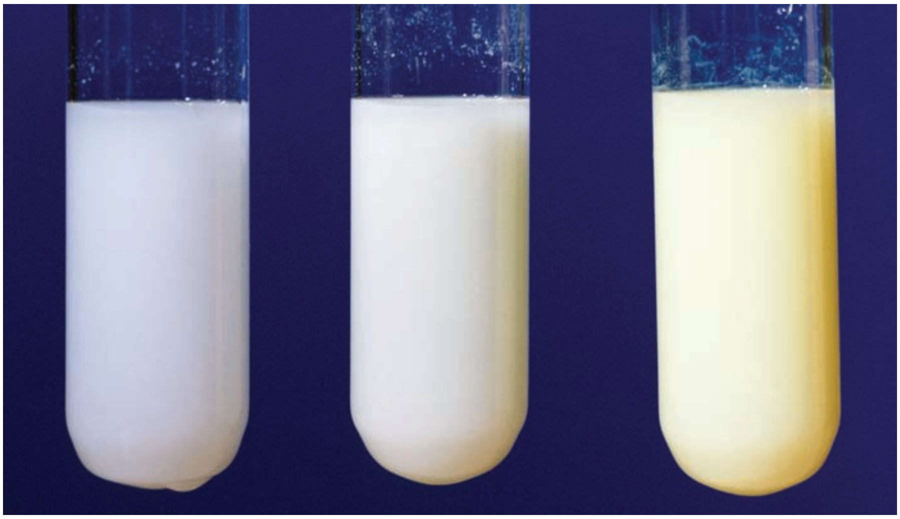


Figure 4.27 Precipitates of silver chloride, silver bromide and silver iodide formed by adding silver nitrate solution to solutions of the halide ions.

Key term

Displacement reactions are redox reactions which can be used to compare the relative strengths of metals as reducing agents and non-metals as oxidising agents. A more reactive element displaces a less reactive element from one of its salts.

Silver nitrate solution can be used to distinguish between halides (Figure 4.27). Silver fluoride is soluble, so there is no precipitate on adding silver nitrate to a solution of fluoride ions. The other silver halides are insoluble – adding silver nitrate to a solution of one of these halide ions produces a precipitate (Table 4.7). For example:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

Table 4.7 Properties of silver halides.

Silver halide	Observations when aqueous silver nitrate is added to a solution of the halide	Effect of adding aqueous ammonia to a precipitate of the silver halide
Silver chloride, AgCl	White precipitate quickly turns purple–grey in sunlight	Precipitate dissolves easily in dilute ammonia to form a colourless solution
Silver bromide, AgBr	Creamy coloured precipitate	Precipitate dissolves in concentrated aqueous ammonia to form a colourless solution
Silver iodide, AgI	Yellow precipitate	Precipitate does not dissolve in ammonia solution

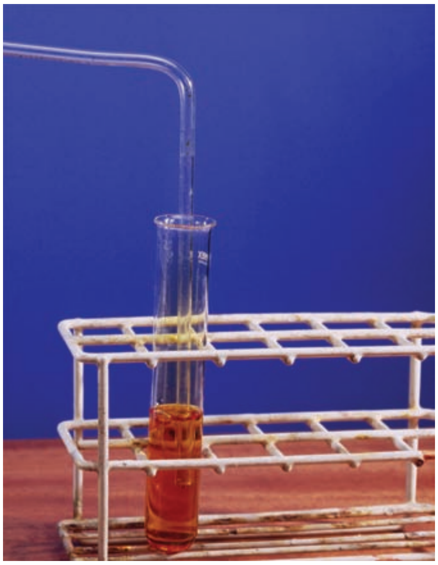


Figure 4.28 Chlorine bubbling through potassium bromide solution. The more reactive chlorine displaces bromine. The aqueous solution of bromine is orange.

In Group 7, a more reactive halogen oxidises the ions of a less reactive halogen. So chlorine displaces bromine from a bromide, while bromine reacts with a solution of an iodide to produce iodine (Figure 4.28). This is an example of a **displacement reaction**. Bromine has a stronger tendency than iodine to gain electrons and turn into ions.

$$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$$

In Group 7, a more reactive halogen displaces a less reaction halogen.

Reactions of halides with concentrated sulfuric acid

Warming solid sodium chloride with concentrated sulfuric acid produces hydrogen chloride gas. This colourless gas produces white fumes in moist air. The acid–base reaction between sodium chloride and sulfuric acid can be used to make hydrogen chloride.

$$NaCl(s) + H_2SO_4(l) \rightarrow HCl(g) + NaHSO_4(s)$$

This type of reaction cannot be used to make pure hydrogen bromide because bromide ions are oxidised to bromine by concentrated sulfuric acid. However the reaction with potassium bromide is used to convert alcohols to bromoalkanes (Section 6.3.8).

Iodide ions are such strong reducing agents that they reduce sulfur from the +6 state in H_2SO_4 to sulfur and hydrogen sulfide (Figure 4.29). This reaction is so rapid that little or no hydrogen iodide is formed. These reactions of halide ions with sulfuric acid show that there is a trend in the strength of the halide ions as reducing agents (Table 4.8).

Table 4.8 Reactions of concentrated sulfuric acid with sodium halides.

Reaction	Observations and products	Type of reaction
NaCl + concentrated H_2SO_4	Colourless acidic gas forms that fumes in moist air (HCl). A white solid remains ($NaHSO_4$).	Acid–base reaction. No redox.
NaBr + concentrated H_2SO_4	Orange vapour (Br_2) mixed with a colourless, acidic gas (SO_2). The solid product is $NaHSO_4$. Some HBr is also formed.	Mainly a redox reaction in which bromide ions are oxidised to bromine. Sulfur is reduced from the +6 to the +4 state. Also an acid–base reaction to form HBr.
NaI + concentrated H_2SO_4	A dark solid forms which gives off a purple vapour on warming (I_2). Some yellow solid may be seen (S) and there is a bad-egg smell (H_2S).	A redox reaction in which iodide ions are oxidised to iodine. Sulfur is reduced from the +6 to the 0 and −2 states.

The trend in the power of the halide ions to act as reducing agents is $I^- > Br^- > Cl^-$. Chlorine is the strongest oxidising agent of these halogens, so it has the greatest tendency to form negative ions. Conversely, chloride ions are reluctant to give up their electrons and turn back into chlorine molecules. So the chloride ion is the weakest reducing agent.

Iodine is the weakest oxidising agent, so it has the least tendency to form negative ions. Conversely, the iodide ion is the strongest reducing agent, being most ready to give up electrons and turn back into iodine molecules.

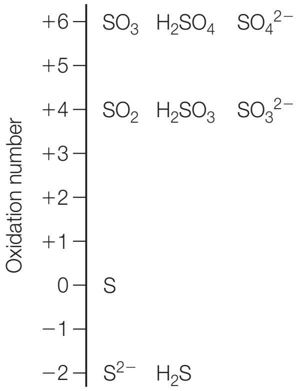


Figure 4.29 The oxidation states of sulfur.

Tip

Hydrogen iodide can be made by warming potassium iodide with concentrated phosphoric acid, H_3PO_4. Phosphoric acid is not an oxidising agent.

Test yourself

36 Draw a diagram of laboratory apparatus for collecting several large test tubes full of hydrogen chloride gas from the reaction of sodium chloride with concentrated sulfuric acid.

37 With the help of oxidation numbers, write a balanced equation for the redox reaction of sodium bromide with concentrated sulfuric acid.

Hydrogen halides

The hydrogen halides are compounds of hydrogen with the halogens. They are all colourless, molecular compounds with the formula HX, where X stands for Cl, Br or I. The bonds between hydrogen and the halogens are polar.

Hydrogen chloride, hydrogen bromide and hydrogen iodide are similar in that they are:

- colourless gases at room temperature which fume in moist air
- very soluble in water, forming acidic solutions (hydrochloric, hydrobromic and hydriodic acids) which ionise completely in water (Figure 4.30)
- strong acids, so they ionise completely in water.

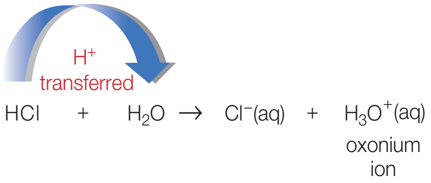


Figure 4.30 The reaction of hydrogen chloride with water. Hydrogen chloride is a strong acid which is fully ionised in aqueous solution.

Mixing any of the hydrogen halides with ammonia produces a white smoke of an ammonium salt (Figure 4.31). Ammonia molecules turn into ammonium ions, NH_4^+, in this reaction. The ammonia is acting as a base by accepting hydrogen ions from the hydrogen halides.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

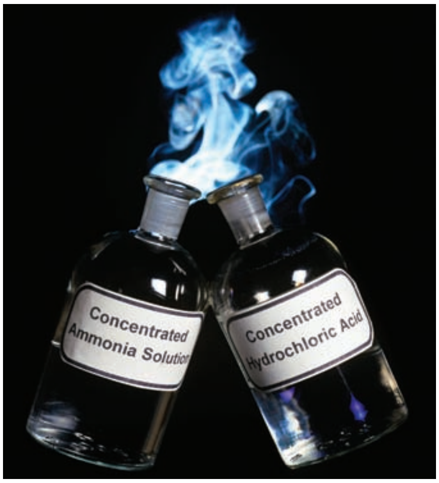


Figure 4.31 Fumes of ammonium chloride forming as gases escaping from concentrated ammonia solution and concentrated hydrochloric acid mix and react. Ammonium chloride is a white solid, while hydrogen chloride and ammonia are colourless gases.

Test yourself

38 Write ionic equations for the reactions of silver nitrate solution with:

a) potassium iodide solution

b) sodium bromide solution.

39 Describe the colour changes on adding:

a) a solution of chlorine in water to aqueous sodium bromide

b) a solution of bromine in water to aqueous potassium iodide.

40 Put the chloride, bromide and iodide ions in order of their strength as reducing agents, with the strongest reducing agent first. Justify your answer.

41 Explain why the compound of hydrogen and fluorine is a liquid at room temperature on a cool day, when the other hydrogen halides are gases.

42 a) Show that the reaction of ammonia with hydrogen bromide gas involves proton transfer.

b) Explain why the product of the reaction is a solid.

4.11 Halogens in oxidation states +1 and +5

Chlorine **oxoanions** form when chlorine reacts with water and alkalis.

Key term

An **oxoanion** is an ion with the general formula is $X_xO_y^{z-}$ (where X represents any element while O represents an oxygen atom).

When chlorine dissolves in water, it reacts reversibly, forming a mixture of weak chloric(I) acid and strong hydrochloric acid. This is an example of a disproportionation reaction (Section 3.4).

$$H_2O(l) + Cl_2(g) \rightarrow HClO(aq) + HCl(aq)$$

Bromine reacts in a similar way but to a much lesser extent. Iodine is insoluble in water and hardly reacts at all.

When chlorine dissolves in potassium (or sodium) hydroxide solution at room temperature it produces chlorate(I) and chloride ions (Figure 4.32).

$$Cl_2(g) + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$$

The active ingredient in household bleach is sodium chlorate(I), made by dissolving chlorine in sodium hydroxide solution.

On heating, the chlorate(I) ions disproportionate to chlorate(V) and chloride ions.

$$\underset{+1}{3ClO^-(aq)} \rightarrow \underset{+5}{ClO_3^-(aq)} + \underset{-1}{2Cl^-(aq)}$$

The overall equation for the reaction of chlorine with hot potassium hydroxide is:

$$3Cl_2(g) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 5Cl^-(aq) + 3H_2O(l)$$

Bromine and iodine react in a similar way to chlorine with alkalis. The BrO^- and IO^- ions are less stable, so they disproportionate at a lower temperature. A hot solution of iodine in potassium hydroxide produces a solution containing potassium iodate(V) and potassium iodide.

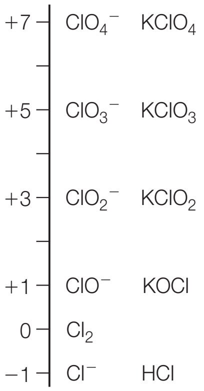


Figure 4.32 The oxidation states of chlorine.

Test yourself

43 a) Write a balanced, ionic equation for the reaction of iodine with hot aqueous hydroxide ions.

b) Use oxidation numbers to show that this is a disproportionation reaction.

Activity

Water treatment

At very low concentrations, chlorine is used to disinfect tap water. It forms chloric(I) acid, HClO, when it reacts with water. Chloric(I) acid is a powerful oxidising agent and a weak acid. It is an effective disinfectant because, unlike ClO^- ions, the molecule can pass through the cell walls of bacteria. Once inside the bacterium, the HClO molecules break the cell open and kill the organism by oxidising and chlorinating molecules which make up its structure.

Chloric(I) acid is a weak acid. It is only very slightly ionised in solution. The concentration of un-ionised HClO in a solution depends on the pH, as shown in Figure 4.33.

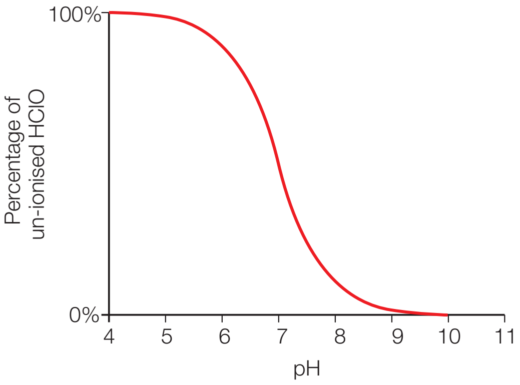


Figure 4.33 Graph to show how the concentration of chloric(I) acid, HClO, varies over a range of pH values at 20 °C.

Swimming pools can be sterilised with much higher concentrations of chlorine compounds which react to produce chloric(I) acid when they dissolve in water. Swimming pool managers have to check the pH of the water carefully – they aim to keep the pH in the range 7.2–7.8 (Figure 4.34).

1 Write an equation to show the formation of chloric(I) acid when chlorine reacts with water.

2 Swimming pools used to be treated with chlorine gas from cylinders containing the liquefied gas under pressure. Now they are usually treated with chemicals that are supplied as solids and that produce chloric(I) acid when added to water. Suggest reasons for this change.

3 Explain why sodium chlorate(I) produces chloric(I) acid when added to water at pH 7–8.

4 Explain why the pH of swimming pool water must not be allowed to rise above 7.8.

5 Suggest reasons why pool water must not become acidic, even though this would increase the concentration of un-ionised HClO.

6 Nitrogen compounds, including ammonia, urea and proteins, react with HClO to form chloramines, which are irritating to skin and eyes. Different chloramines can react to form nitrogen and hydrogen chloride, which gets rid of the problem. However, if there is excess HClO, another reaction produces nitrogen trichloride, which is responsible for the so-called 'swimming pool smell'. Nitrogen trichloride is very irritating to skin and eyes. Write equations to show:

a) the formation of the chloramine, NH_2Cl, from ammonia and chloric(I) acid

b) the removal of chloramines by reaction of NH_2Cl with $NHCl_2$

c) the formation of nitrogen trichloride from chloramine, NH_2Cl.

7 Explain why swimming pools do not smell of chlorine if they are properly maintained.

Figure 4.34 Chlorine compounds treat the water in swimming pools.

Exam practice questions

1 The elements Mg to Ba in Group 2, and their compounds, can be used to show the trends in properties down a group of the periodic table. State and explain the trend down the group in:

a) atomic radius *(3)*

b) first ionisation energy *(3)*

c) thermal stability of the carbonates. *(3)*

2 a) Write an equation for the reaction of chlorine with aqueous sodium hydroxide, and use this example to explain what is meant by disproportionation. *(2)*

b) On heating, chlorate(I) ions in solution disproportionate to chlorate(V) ions and chloride ions. Write an ionic equation for this reaction. *(2)*

c) On heating to just above its melting temperature, $KClO_3$ reacts to form $KClO_4$ and KCl. Write a balanced equation for the reaction and show that it is a disproportionation reaction. *(3)*

3 Identify the following salts and account for the observations.

a) X is a white solid which colours a flame bright yellow. No precipitate forms on mixing a solution of X with sodium hydroxide solution. On heating, X gives off a colourless gas that relights a glowing splint. *(4)*

b) Y is a white, crystalline solid which colours a flame green. Adding dilute nitric acid followed by silver nitrate solution to a solution of Y produces a white precipitate. *(2)*

c) Z is a white crystalline solid which colours a flame lilac. Z is soluble in water – the solution does not change the colour of indicators. Mixing the solution with a solution of silver nitrate produces a cream precipitate that is insoluble in dilute aqueous ammonia but soluble in concentrated aqueous ammonia. A solution of Z turns orange on adding aqueous chlorine. *(4)*

● **4** Radium is a highly radioactive element which is below barium in the periodic table. Use your knowledge of the chemistry of the elements Mg to Ba in Group 2 to predict properties of radium and its compounds. Include in your predictions a description of the following changes, equations for any chemical changes and the appearance of the products:

a) the reaction of radium with oxygen *(3)*
b) the reaction of radium with water *(3)*
c) the reaction of radium oxide with water *(3)*
d) the reaction of radium hydroxide with dilute hydrochloric acid *(3)*
e) the solubility of radium sulfate in water *(2)*
f) the effect of heating radium nitrate. *(3)*

● **5** This generalisation is sometimes stated for the ionic compounds of Group 2 elements:

'For Group 2 compounds with small anions solubility in water increases down the group; for compounds with large anions solubility decreases down the group.'

a) Discuss, with the help of examples, whether or not this generalisation can be justified. *(6)*

b) Would you expect magnesium fluoride to be more or less soluble than barium fluoride? *(2)*

● **6** Astatine, At, is the element below iodine in Group 7. Predict, giving your reasons:

a) the physical state of astatine at room temperature *(3)*

b) the effect of bubbling chorine though an aqueous solution of sodium astatide *(2)*

c) whether or not hydrogen astatide forms on adding concentration sulfuric acid to solid sodium astatide *(3)*

d) the colour of silver astatide and its solubility in concentrated ammonia solution. *(2)*

● **7** Describe the observations and write equations to explain how each of the following reagents can be used to distinguish between sodium bromide and sodium iodide. Include in your answer any additional tests that help to confirm the interpretation of observations:

a) aqueous chlorine *(6)*
b) aqueous silver nitrate *(6)*
c) concentrated sulfuric acid. *(6)*

● **8** State the trend in the power of chloride, bromide and iodide ions as reducing agents. Describe how you could demonstrate the trend by carrying out experiments in the laboratory. Include in your description the main observations that illustrate the differences between the ions. Include equations for the reactions. *(6)*

● **9 a)** Hydrogen fluoride is manufactured by heating concentrated sulfuric acid with fluorite, CaF_2, obtained by purifying the mineral fluorspar. Hydrogen fluoride leaves the kiln as a gas. It can be condensed to a liquid and purified by fractional distillation. The other product formed in the kiln is solid calcium sulfate.

i) Write an equation for the reaction in the kiln. *(1)*

ii) Why is it much easier to condense hydrogen fluoride to a liquid than the other hydrogen halides? *(3)*

b) Hydrogen chloride was traditionally made by adding concentrated sulfuric acid to sodium chloride. Today, the main, industrial source of hydrogen chloride is as a co-product of processes in the petrochemical industry, such as the chlorination of hydrocarbons. A small amount of the gas is made by the reaction between the hydrogen and chlorine produced during the manufacture of sodium hydroxide during the electrolysis of aqueous sodium chloride. This is used to make the purest hydrochloric acid.

i) Explain why the chlorination of hydrocarbons is a source of hydrogen chloride and suggest reasons why 90% of the gas is now produced by the petrochemical industry. *(3)*

ii) Why does the manufacture of sodium hydroxide also produce hydrogen and chlorine? Suggest reasons why the gases made in this way are very pure. *(2)*

iii) Why does the reaction of hydrogen gas with chlorine gas have to be very carefully controlled when it is used to manufacture hydrochloric acid? *(1)*

iv) Suggest an example to show why it is sometimes important for chemists to use very pure hydrochloric acid. *(1)*

c) Hydrogen bromide is manufactured on a much smaller scale than hydrogen chloride. Why is hydrogen bromide not made by adding concentrated sulfuric acid to a bromide, such as sodium bromide? *(2)*

10 The table at the bottom of the page compares properties of the chlorides of Group 2 elements.

a) What is the evidence from the data that the bonding and structure of beryllium chloride differ from the bonding and structure of the chlorides of other elements in Group 2? *(2)*

b) Suggest an explanation for the differences identified in (a). *(4)*

c) In the gas phase, beryllium chloride is molecular. Explain why beryllium chloride molecules have a linear shape. *(3)*

d) In the solid state, $BeCl_2$ molecules polymerise to make long chains. Explain, with the help of a diagram, how these chains can form by beryllium forming four bonds with chlorine atoms arranged tetrahedrally around each Be atom. *(4)*

11 Solid iodine reacts with excess liquid chlorine at a low temperature. A yellow solid remains after evaporating the excess chlorine. The formula of the solid is ICl_x. One mole of ICl_x reacts with excess potassium iodide solution to form four moles of iodine, I_2. Determine the value of x and write equations for the two reactions. Identify the molecules or ions that are oxidised or reduced in the reactions. *(6)*

12 A mixture of two solid potassium halides was investigated in two ways.

A A sample of the mixture was dissolved in water to make a concentrated solution. Chlorine gas was bubbled through the solution until there was no further reaction. A dark grey precipitate formed and orange-brown fumes appeared above the solution.

B A 0.214 g sample of the mixture was dissolved in water. An excess of silver nitrate solution was added. The precipitate that formed was separated washed and dried. The mass of precipitate was 0.317 g. Next, the precipitate was treated with concentrated ammonia solution. Some of the precipitate dissolved. After separating, washing and drying again, the mass of precipitate reduced to 0.176 g.

a) What can you deduce from the observations in A? *(3)*

b) Write ionic equations for the reactions that led to the observations described. (2)

c) Use the data from B to determine the percentage by mass of the two potassium halides in the original mixture. Show how you arrive at your answer. *(6)*

Compound	**Melting temperature/°C**	**Boiling temperature/°C**	**Solubility in mol/100 g water**
Beryllium chloride, $BeCl_2$	450	520	0.19
Magnesium chloride, $MgCl_2$	714	1412	0.56
Calcium chloride, $CaCl_2$	782	2000	0.54
Strontium chloride, $SrCl_2$	911	1250	0.01
Barium chloride, $BaCl_2$	963	1560	0.15

5 Formulae, equations and amounts of substance

5.1 Understanding chemical quantities

Chemists often need to measure how much of a particular chemical there is in a sample. Analysts in pharmaceutical companies, for example, test samples of tablets and medicines to check that they contain the right amount of a drug. Industrial chemists measure the amounts of substances they need for chemical processes. Laboratory chemists calculate the yield of product they expect when they mix measured quantities of the reactants for a synthesis. In these, and many other contexts, chemists have to be able to measure amounts of substances accurately.

Key terms

Amount of substance is a physical quantity (symbol n) which is measured in the unit mole (symbol mol).

Relative atomic mass, A_r, is the average mass of an element relative to $\frac{1}{12}$th of the mass of an atom of the isotope carbon-12. The values are relative so they do not have units.

Molar mass is the mass of one mole of a chemical – the unit is g mol^{-1}. As always with molar amounts, the symbol or formula of the chemical must be specified.

Chemical amounts

In chemistry, the **amount of a substance** is measured in moles. Chemists use the unit 'mole' to measure an amount of substance containing a standard number of atoms, molecules or ions. The word 'mole' entered the language of chemistry at the end of the nineteenth century. It is based on the Latin word for a heap or a pile.

When chemists are determining formulae or working with equations, they need to measure amounts in moles. Chemists have balances to measure masses and graduated containers to measure volumes, but there is no instrument for measuring chemical amounts directly. Instead, chemists must first measure the masses or volumes of substances and then calculate the chemical amounts.

Molar masses

The key to working with chemical amounts in moles is to know the relative masses of different atoms. The accurate method for determining **relative atomic masses** involves the use of a mass spectrometer (Section 1.3).

One mole of an element has a mass that is equal to its relative atomic mass in grams. So, the mass of one mole of carbon is 12.0 g and the mass of one mole of copper is 63.5 g. These masses of one mole are called **molar masses** (symbol M). So, the molar mass of carbon, $M(\text{C}) = 12.0$ g mol^{-1} and the molar mass of copper, $M(\text{Cu}) = 63.5$ g mol^{-1} (Figure 5.1).

Similarly the molar mass of the molecules of an element or a compound is numerically equal to its relative molecular mass. So, the molar mass of oxygen molecules, $M(\text{O}_2) = 32.0$ g mol^{-1} and the molar mass of sulfuric acid, $M(\text{H}_2\text{SO}_4) = 98.1$ g mol^{-1}. Likewise, the molar mass of an ionic compound is numerically equal to its relative formula mass. The molar mass of sodium chloride, NaCl, is therefore 58.5 g mol^{-1} (Figure 5.2).

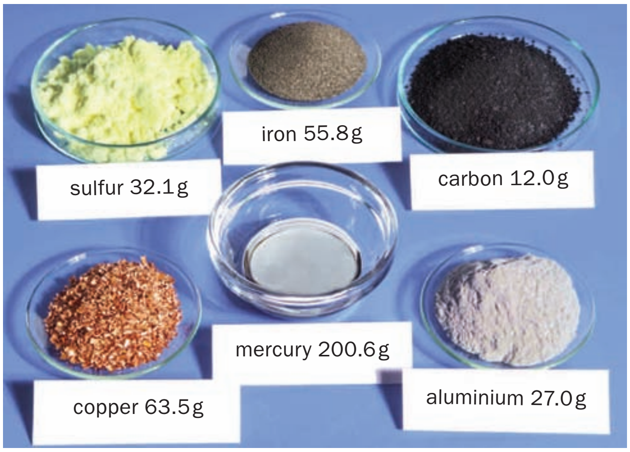

iron 55.8 g
sulfur 32.1 g
carbon 12.0 g
mercury 200.6 g
copper 63.5 g
aluminium 27.0 g

Figure 5.1 One mole amounts of copper, carbon, iron, aluminium, mercury and sulfur.

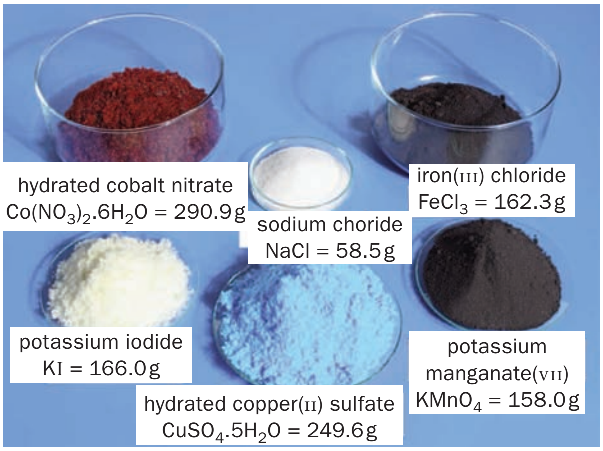

hydrated cobalt nitrate
$Co(NO_3)_2.6H_2O$ = 290.9 g
sodium choride
$NaCl$ = 58.5 g
iron(III) chloride
$FeCl_3$ = 162.3 g
potassium iodide
KI = 166.0 g
hydrated copper(II) sulfate
$CuSO_4.5H_2O$ = 249.6 g
potassium manganate(VII)
$KMnO_4$ = 158.0 g

Figure 5.2 One mole amounts of some ionic compounds.

Amount in moles

Tip

Section A1.1 of Appendix A1 gives advice on how to work out the value of maths equations with brackets and combinations of multiplication and addition.

The mole is the SI unit for amount of substance. The name of the quantity is 'mole'. Its unit is 'mol'. So,

12 g of carbon contains 1 mol of carbon atoms

24 g of carbon contains 2 mol of carbon atoms

240 g of carbon contains 20 mol of carbon atoms.

Notice that:

$$\text{amount of substance/mol} = \frac{\text{mass of substance/g}}{\text{molar mass/g mol}^{-1}}$$

Key term

The term **species** is a useful collective noun used by chemists to refer generally to atoms, molecules or ions.

It is important to be precise about the chemical **species** involved when measuring amounts in moles. In calcium chloride, $CaCl_2$, for example, there are two chloride ions, Cl^-, combined with each calcium ion, Ca^{2+}. So in one mole of calcium chloride there is one mole of calcium ions and two moles of chloride ions.

Tip

Section A1.5 of Appendix A1 gives help with substituting values into mathematical formulae.

The Avogadro constant

Relative atomic masses show that one atom of carbon is 12 times heavier than one atom of hydrogen. This means that 12 g of carbon contains the same number of atoms as 1 g of hydrogen. Similarly, one atom of oxygen is 16 times as heavy as one atom of hydrogen, so 16 g of oxygen also contains the same number of atoms as 1 g of hydrogen.

Key term

The **Avogadro constant** is the number of atoms, molecules or ions in one mole of a substance. The constant has the unit mol^{-1}.

In fact, the molar mass of every element (1 g of hydrogen, 12 g carbon, 16 g oxygen, and so on) contains the same number of atoms. This number is called the **Avogadro constant**, after the Italian scientist Amedeo Avogadro. Experiments show that the Avogadro constant, L, is $6.02 \times 10^{23}\,\text{mol}^{-1}$. Written out in full this is 602 000 000 000 000 000 000 000 atoms, molecules or ions per mole.

The Avogadro constant is the number of atoms, molecules or formula units in one mole of any substance. So, one mole of oxygen (O_2) contains 6.02×10^{23} O_2 molecules and two moles of oxygen (O_2) contains $2 \times 6.02 \times 10^{23}$ O_2 molecules.

$$\text{The number of atoms, molecules or formula units} \\ = \text{amount of chemical/mol} \times \text{the Avogadro constant/mol}^{-1}$$

Again, it is vital to specify the chemical species concerned in calculating the amount of a substance or the number of particles in a sample of a substance. For example, 2 g of hydrogen contains 2 mol of hydrogen (H) atoms (12.04×10^{23} atoms) but only 1 mol of hydrogen (H_2) molecules (6.02×10^{23} molecules).

Test yourself

1 What is the amount, in moles, of:

- **a)** 20.05 g of calcium atoms
- **b)** 3.995 g of bromine atoms
- **c)** 159.8 g of bromine molecules
- **d)** 6.41 g of sulfur dioxide molecules
- **e)** 10.0 g of sodium hydroxide?

2 What is the mass of:

- **a)** 0.1 mol of iodine atoms
- **b)** 0.25 mol of chlorine molecules
- **c)** 2.0 mol of water molecules
- **d)** 0.01 mol of ammonium chloride, NH_4Cl
- **e)** 0.125 mol of sulfate ions, SO_4^{2-}?

3 How many moles of:

- **a)** sodium ions are there in 1 mol of sodium carbonate, Na_2CO_3
- **b)** bromide ions are there in 0.5 mol of barium bromide, $BaBr_2$
- **c)** nitrogen atoms are there in 2 mol of ammonium nitrate, NH_4NO_3?

4 Use the Avogadro constant to calculate:

- **a)** the number of chloride ions in 0.5 mol of sodium chloride, NaCl
- **b)** the number of oxygen atoms in 2 mol of oxygen molecules, O_2
- **c)** the number of sulfate ions in 3 mol of aluminium sulfate, $Al_2(SO_4)_3$.

5.2 Finding empirical formulae

Although the formulae of most compounds can be predicted, the only sure way of determining the formula of a substance is by experiment. This has been done for all common compounds and their formulae can be checked in tables of data.

'Empirical' evidence is information based on experience or experiment, so chemists use the term **empirical formulae** for formulae calculated from the results of experiments.

An experiment to find an empirical formula involves measuring the masses of elements which combine in the compound. From these masses, it is possible to calculate the number of moles of atoms which react, and hence the ratio of atoms which react. This gives an empirical formula which shows the simplest whole number ratio for the atoms of different elements in a compound.

Key term

An **empirical formula** shows the simplest whole number ratio of the atoms of different elements in a compound; for example, CH_4 for methane and CH_3 for ethane.

Tip

Section A1.4 of Appendix A1 gives help with calculations involving ratio and proportion.

Example

Analysis of 20.1 g of an iron bromide sample showed that it contained 3.80 g of iron and 16.3 g of bromine. What is its empirical formula?

Notes on the method

The molar masses of the elements come from the periodic table (see page 314).

Convert the masses in grams to amounts in moles by dividing by the molar masses of the atoms of the elements.

Divide the amounts by the smaller of the amounts to find the simplest whole number ratio.

Answer

	iron	**bromine**
Combined masses	3.80 g	16.3 g
Molar mass	$55.8\,\text{g}\,\text{mol}^{-1}$	$79.9\,\text{g}\,\text{mol}^{-1}$
Combined moles of atoms	$\frac{3.80\,\text{g}}{55.8\,\text{g}\,\text{mol}^{-1}} = 0.0681\,\text{mol}$	$\frac{16.3\,\text{g}}{79.9\,\text{g}\,\text{mol}^{-1}} = 0.204\,\text{mol}$
Ratio of combined atoms	$\frac{0.0681}{0.0681} = 1.00$	$\frac{0.204}{0.0681} = 2.996 = 3.00$

Simplest whole number ratio of atoms is 1 : 3

So, the empirical formula is $FeBr_3$.

Key term

Percentage composition is the percentage by mass of each of the elements in a sample of a compound.

Percentage composition

Sometimes, the results of an analysis of a compound show the percentages of the different elements, rather than their masses. This is the **percentage composition** of the compound. The empirical formula of the compound can be calculated from these results.

Example

What is the empirical formula of copper pyrites which has the analysis 34.6% copper, 30.5% iron and 34.9% sulfur by mass?

Notes on the method

Follow the procedure in the example for finding an empirical formula. The percentages, in effect, show the combining masses in a 100 g sample of the compound.

Answer

	copper	**iron**	**sulfur**
Combining masses	34.6 g	30.5 g	34.9 g
Molar masses of elements	$63.5\,\text{g}\,\text{mol}^{-1}$	$55.8\,\text{g}\,\text{mol}^{-1}$	$32.1\,\text{g}\,\text{mol}^{-1}$
Amounts combined	$\frac{34.6\,\text{g}}{63.5\,\text{g}\,\text{mol}^{-1}}$ $= 0.545\,\text{mol}$	$\frac{30.5\,\text{g}}{55.8\,\text{g}\,\text{mol}^{-1}}$ $= 0.546\,\text{mol}$	$\frac{34.9\,\text{g}}{32.1\,\text{g}\,\text{mol}^{-1}}$ $= 1.09\,\text{mol}$

Simplest whole number ratio of amounts is 1 : 1 : 2

The empirical formula is $CuFeS_2$.

Test yourself

5 What is the empirical formula of the compound in which:

a) 0.60 g carbon combines with 0.20 g hydrogen

b) 1.02 g vanadium combines with 2.84 g chlorine

c) 1.38 g sodium combines with 0.96 g sulfur and 1.92 g oxygen?

6 What is the empirical formula of the compound in which the percentages by mass of the elements present are:

a) 2.04% hydrogen, 32.65% sulfur and 65.31% oxygen

b) 52.18% carbon, 13.04% hydrogen and 34.78% oxygen?

Activity

Finding the formula of red copper oxide

A group of students investigated the formula of red copper oxide by reducing it to copper using natural gas as shown in Figure 5.3.

The experiment was carried out five times, starting with different amounts of red copper oxide. The results are shown in Table 5.1.

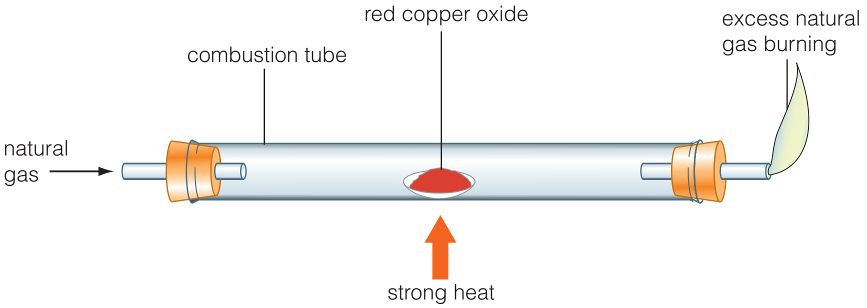


Figure 5.3 Reducing red copper oxide by heating in natural gas.

Table 5.1

Experiment number	Mass of red copper oxide/g	Mass of copper in the oxide/g
1	1.43	1.27
2	2.14	1.90
3	2.86	2.54
4	3.55	3.27
5	4.29	3.81

1 Look at Figure 5.3. What safety precautions should the students take during the experiments?

2 What steps should the students take to ensure that all the copper oxide is reduced to copper?

3 Start a spreadsheet program on a computer and open up a new spreadsheet for your results. Enter the experiment numbers and the masses of copper oxide and copper in the first three columns of your spreadsheet, as in Table 5.1.

4 **a)** Enter a formula in column 4 to work out the mass of oxygen in the red copper oxide used.

b) Enter a formula in column 5 to find the amount of copper in moles in the oxide.

c) Enter a formula in column 6 to find the amount of oxygen in moles in the oxide.

5 From the spreadsheet, plot a line graph of amount of copper (*y*-axis) against amount of oxygen (*x*-axis). Print out your graph. If you cannot plot graphs directly from the spreadsheet, draw the graph by hand.

6 Which of the points should be disregarded in drawing the line of best fit?

7 **a)** What, from your graph, is the average value of the ratio:

$$\frac{\text{amount of copper/mol}}{\text{amount of oxygen/mol}}?$$

b) How much copper, in moles, combines with one mole of oxygen in red copper oxide?

c) What is the formula of red copper oxide?

8 Give reasons why the students could claim that their answer for the formula of the oxide was valid?

9 Write a word equation, and then a balanced equation, for the reduction of red copper oxide to copper using methane (CH_4) in natural gas. (Hint: The only solid product is copper.)

Key terms

The **gas laws** describe the behaviour of gases and are summarised by the ideal gas equation.

Ideal gases are gases which obey the ideal gas equation. In practice, real gases deviate to at least some extent from ideal behaviour.

SI units are the internationally agreed units for measurement in science.

Pressure is defined as force per unit area. The SI unit of pressure is the pascal (Pa) which is a pressure of one newton per square metre ($1\,N\,m^{-2}$). The pascal is a very small unit and so pressures are often quoted at kilopascals (kPa). Atmospheric pressure is measured in bar:

1 bar = 100 000 Pa = 100 kPa

Volume is the amount of space taken up by a sample. The SI unit of volume is the cubic metre (m^3). Chemists generally measure volumes in cubic decimetres (dm^3) or cubic centimetres (cm^3): 1 dm = 10 cm and so $1\,dm^3 = 10\,cm \times 10\,cm \times 10\,cm = 1000\,cm^3$; $1\,dm^3$ is the same volume as a litre; $1\,m = 10\,dm$ so $1\,m^3 = 10^3\,dm^3 = 10^6\,cm^3$.

The **kelvin** is the SI unit of temperature on the absolute, or Kelvin, temperature scale. On this scale, absolute zero is 0 K, water freezes at 273 K and boils at 373 K.

Test yourself

7 What are the values of these temperatures on the Kelvin scale?

a) boiling temperature of nitrogen, −196 °C

b) boiling temperature of butane, −0.5 °C

c) melting temperature of sucrose, 186 °C

d) melting temperature of iron, 1540 °C

5.3 Amounts of gases

Gases and the gas laws

The Irish chemist Robert Boyle (1627–91) was one of the first people to investigate the effect of pressure on the volume of gases. About a hundred years after, in the late 18th century, the hot air balloon flights of the Montgolfier brothers stimulated scientists to study the behaviour of gases. Two of these scientists were French: Joseph Gay-Lussac (1778–1850) and Jacques Charles (1746–1823). They were particularly interested in the variation of the volumes of gases with temperature. Jacques Charles put his theories to the test and in 1783 made the first ascent in a hydrogen balloon. Meanwhile, the Italian scientist Amedeo Avogadro (1776–1856) proposed the law that equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules.

These scientists discovered the **gas laws** that show how the volume, V, of a sample of gas depends on three things:

- the temperature, T
- the pressure, p
- the amount of gas in moles, n.

Real and ideal gases

Scientists use the concept of an '**ideal gas**' which obeys the gas laws perfectly. In practice, real gases do not obey the laws under all conditions. Under laboratory conditions, however, there are gases which are close to behaving like an ideal gas. These are the gases which, at room temperature, are well above their boiling points, such as helium, nitrogen, oxygen and hydrogen.

Chemists generally find that the gas laws predict the behaviour of real gases accurately enough to make them a useful practical guide, but it is important to bear in mind that gases such as ammonia, butane, sulfur dioxide and carbon dioxide can show marked deviations from ideal behaviour. These are the gases which boil only a little below room temperature and can be liquefied just by raising the pressure.

The ideal gas equation

The behaviour of an ideal gas can be summed up by combining the gas laws into a single equation called the ideal gas equation:

$$pV = nRT$$

When **SI units** are used, the **pressure** is measured in pascals, Pa, the **volume** in cubic metres, m^3, and the temperature in **kelvin**, K. R, in the ideal gas equation, is the gas constant. R has the value $8.31\,J\,mol^{-1}\,K^{-1}$ if all quantities are in SI units.

Measuring molar masses of gases

In the days before mass spectrometry (Section 1.3) chemists used the ideal gas equation to measure the molar masses of gases and of other substances that evaporate easily. The method is accurate enough to determine the **molecular formula** of elements and compounds.

One practical approach is to inject a weighed sample of a liquid into a syringe heated in an oven. Measurements taken include the volume of vapour, the temperature of the vapour and its pressure (the atmospheric pressure). Measurements are converted to SI units and then substituted in the ideal gas equation to find the amount in moles, *n*.

Key term

The **molecular formula** gives the actual number of atoms of each element in a molecule.

Example

A 0.124 g sample of a liquid with the empirical formula C_3H_7 evaporates to give 45.0 cm3 vapour at 100 °C and a pressure of 100 kPa. What is the molecular formula of the liquid?

Notes on the method

Convert all units to SI units: $1\,\text{cm}^3 = 10^{-6}\,\text{m}^3$.

Substitute in the equation $pV = nRT$ to find *n* (the amount in moles).

The equation rearranges to give: $n = \dfrac{pV}{RT}$

The molar mass can then be calculated by dividing the mass of the sample in grams by the amount in moles, giving an answer with the units g mol^{-1}.

Answer

For the sample of liquid:

- pressure = $100\,000\,\text{N m}^{-2}$
- volume = $45.0 \times 10^{-6}\,\text{m}^3$
- temperature = 373 K

The gas constant = $8.31\,\text{J mol}^{-1}\,\text{K}^{-1}$

$$n = \frac{pV}{RT} = \frac{100\,000\,\text{Pa} \times 45.0 \times 10^{-6}\,\text{m}^3}{8.31\,\text{J mol}^{-1}\,\text{K}^{-1} \times 373\,\text{K}} = 1.45 \times 10^{-3}\,\text{mol}$$

Mass of the sample = 0.124 g

The amount of substance in the sample = 1.45×10^{-3} mol

Therefore, the molar mass of the liquid = $\dfrac{0.124\,\text{g}}{1.45 \times 10^{-3}\,\text{mol}} = 85.5\,\text{g mol}^{-1}$

A molecular formula is always a simple multiple of the empirical formula (Section 6.1.3).

The relative mass of the empirical formula of the liquid,

$M_r(C_3H_7) = (3 \times 12.0) + (7 \times 1.0) = 43.0$

Even though the vapour of the compound does not behave as an ideal gas, the result is accurate enough to show that the molecular formula is twice the empirical formula. The molecular formula of the compound is C_6H_{14}.

Tip

Including the units at every stage of the calculation is a useful check that the steps have been carried out correctly. The units should cancel to give the expected units for the answer (in this example, mol). To check the units in the ideal gas equation you need to remember that a pressure of 1 Pa = $1\,\text{N m}^{-2}$ and that an energy transfer of 1 J = 1 N m (force times distance).

Tip

Section A1.5 of Appendix A1 gives help with rearranging mathematical equations.

Test yourself

8 The mass of $200\,\text{cm}^3$ of a gaseous hydrocarbon is 0.356 g at 298 K and 100 kPa. What is the molar mass of the gas?

9 A 0.163 g sample of a liquid evaporates to give $65.0\,\text{cm}^3$ of vapour at 101 °C and 100 kPa. What is the molar mass of the liquid?

Key term

The **molar volume** of a gas is the volume of 1 mol of the gas under stated conditions. At room temperature and atmospheric pressure, the molar volume of all gases is 24.0 $dm^3\,mol^{-1}$.

The molar volume of gases

The ideal gas equation shows that, at a fixed temperature and fixed pressure, the volume of a gas depends only on the amount of gas in moles; the type or the formula of the gas does not matter. This is only strictly true for ideal gases but is nevertheless useful when dealing with real gases.

Substituting in the ideal gas equation makes it possible to calculate the volume of one mole of gas under any conditions. This shows that the volume of one mole of any gas occupies about 24 dm^3 (24 000 cm^3) at a typical room temperature of around 16 °C (298 K) and at atmospheric pressure (100 kPa). This volume of one mole of gas is called the **molar volume** under the stated conditions.

So, 1 mole of oxygen (O_2) and 1 mole of carbon dioxide (CO_2) each occupy 24 dm^3 at room temperature. Therefore 2 moles of O_2 occupy 48 dm^3 and 0.5 moles of O_2 occupy 12 dm^3 at room temperature. Notice from these simple calculations that:

$$\text{volume of gas/cm}^3 = \text{amount of gas/mol} \times \text{molar volume/cm}^3\,\text{mol}^{-1}$$

So, under laboratory conditions at room temperature:

$$\text{volume of gas/cm}^3 = \text{amount of gas/mol} \times 24\,000/\text{cm}^3\,\text{mol}^{-1}$$

Activity

Measuring the molar volumes of three gases

The syringe shown in Figure 5.4 is used in an experiment to measure the molar volume of several gases. The procedure is outlined in steps A–I. Sample results are given in Table 5.2.

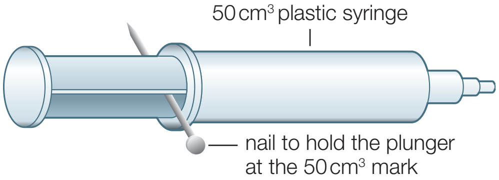


Figure 5.4 Plastic syringe with nail to lock the plunger at the 50 cm^3 mark.

A Remove the nail. Fill the syringe to the 50 cm^3 mark. Seal the syringe with a syringe cap. Check that the plunger returns to the 50 cm^3 mark after pushing in the plunger by 10 cm^3 and releasing, and after pulling out the plunger by 10 cm^3 and releasing.
B Push in the plunger to empty the syringe. Block the nozzle with a syringe cap.
C Pull out the plunger. Lock it at the 50 cm^3 mark with the nail.
D Measure and record the mass of the syringe, syringe cap and nail using a three-place balance.
E Remove the syringe cap and the nail from the plunger. Push in the plunger completely.
F Draw 50 cm^3 gas into the syringe from a plastic bag containing one of the gases.
G Seal the syringe again and use the nail to lock the syringe.
H Measure and record the mass of the syringe, cap and nail.
I Flush out the gas and repeat the procedure with another gas.

Table 5.2 Results recorded at room temperature and pressure.

	Mass/g
Syringe + cap + nail (step D)	142.213
Syringe + cap + nail + carbon dioxide	142.302
Syringe + cap + nail + methane	142.247
Syringe + cap + nail + butane	142.322

1. Explain the purpose of step A.
2. At the end of step C, what is in the syringe and why is it necessary to lock the plunger with the nail?
3. Why is the syringe weighed in step B with the plunger pulled out, rather than weighing the empty syringe with the plunger pushed in?
4. How might a bag be filled with a dry sample of carbon dioxide if the gas is not available from a cylinder? Why must the gas be dry?
5. Use the results in Table 5.2 to determine the molar volumes of the three gases.
6. Why is it necessary to use a three-place balance to measure the masses?
7. What are the main sources of measurement uncertainty in this experiment?
8. How might the procedure be modified to reduce the measurement uncertainty in the results?

5.4 Calculations from equations

An equation is more than a useful shorthand for describing what happens during a reaction. In industry, in medicine and anywhere that chemists make products from reactants, it is vitally important to know the amounts of reactants that are needed for a chemical process and the amount of product that can be obtained. Chemists can calculate these amounts using equations.

Calculating the masses of reactants and products

There are four key steps in solving problems using equations.

Step 1: Write the balanced equation for the reaction.

Step 2: Write down the amounts in moles of the relevant reactants and products in the equation.

Step 3: Convert these amounts in moles of the relevant reactants and products to masses.

Step 4: Scale the masses to the quantities required.

Example

What mass of iron can be obtained from 1.0 kg of iron(III) oxide (iron ore)?

Notes on the method

Only do the calculation for the substances in the equation that affect the answer. In this instance, the CO and CO_2 can be ignored.

In Step 2, you obtain the numbers of moles from the numbers in front of the formulae for the substances. The number is '1' if there is no number in front of the formula.

Look up the relative atomic masses of the elements in the periodic table so that you can work out the molar masses.

The proportions are the same whether the mass of iron oxide is 1.0 g or 1.0 kg (1000 g).

Answer

Step 1: $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

Step 2: $1\,\text{mol}\ Fe_2O_3 \rightarrow 2\,\text{mol}\ Fe$

Step 3: $M(Fe_2O_3) = (2 \times 55.8\,\text{g mol}^{-1}) + (3 \times 16.0\,\text{g mol}^{-1})$

$= 111.6 + 48.0 = 159.6\,\text{g mol}^{-1}$

So, $159.6\,\text{g}\ Fe_2O_3 \rightarrow 2 \times 55.8\,\text{g}\ Fe = 111.6\,\text{g}\ Fe$

Step 4: $159.6\,\text{g}\ Fe_2O_3 \rightarrow 111.6\,\text{g}\ Fe$

$$1.0\,\text{g}\ Fe_2O_3 \rightarrow \frac{111.6}{159.6}\,\text{g}\ Fe$$

$= 0.70\,\text{g}\ Fe$ (giving the answer to two significant figures)

Scaling up, 1.0 kg of iron(III) oxide produces 0.70 kg of iron.

Test yourself

10 What is the amount, in moles, of each gas at room temperature and pressure?

a) $240\,000\,\text{cm}^3$ chlorine

b) $48\,\text{cm}^3$ hydrogen

c) $3.0\,\text{dm}^3$ ammonia

11 What is the volume in cm^3 of each amount of gas at room temperature and pressure?

a) 2.0 mol nitrogen

b) 0.00020 mol neon

c) 0.125 mol carbon dioxide

Test yourself

12 What mass of calcium oxide, CaO, forms when 25 g calcium carbonate, $CaCO_3$, decomposes on heating?

13 What mass of sulfur combines with 8.0 g copper to form copper(I) sulfide, Cu_2S?

14 What mass of sulfur is needed to produce 1.0 kg of sulfuric acid, H_2SO_4?

Measuring the volumes of gases in reactions

The apparatus in Figure 5.5 can be used to measure the reacting volumes of dry ammonia gas (NH_3) and dry hydrogen chloride gas (HCl).

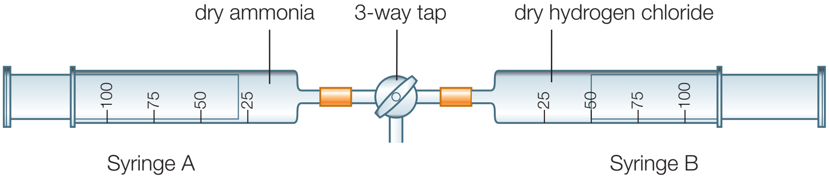


Figure 5.5 Measuring the reacting volumes of ammonia and hydrogen chloride.

When 30 cm^3 of ammonia gas and 50 cm^3 of hydrogen chloride gas are mixed, ammonium chloride (NH_4Cl) forms as a white solid. The volume of this solid is insignificant compared to the volume of the gases. The volume of gas remaining is 20 cm^3, which turns out to be excess hydrogen chloride.

So,

30 cm^3 of NH_3 reacts with 30 cm^3 of HCl

1 cm^3 of NH_3 reacts with 1 cm^3 of HCl

and 24 dm^3 of NH_3 reacts with 24 dm^3 of HCl.

This shows that 1 mol of NH_3 reacts with 1 mol of HCl.

Notice that the ratio of the reacting volumes of these gases is the same as the ratio of the reacting amounts in moles shown in the equation for the reaction. This is always the case when gases react.

$$\begin{array}{cccl} NH_3(g) & + & HCl(g) & \rightarrow NH_4Cl(s) \\ 1\,\text{mol} & & 1\,\text{mol} & \\ 1\ \text{volume} & & 1\ \text{volume} & \end{array}$$

Gas volume calculations

Gas volume calculations are straightforward when all the relevant substances are gases. In these cases, the ratio of the gas volumes in the reaction is the same as the ratio of the numbers of moles in the equation. This is the case because the volume of a gas, under given conditions of temperature and pressure, depends only on the *amount* of the gas and not on the *type* of gas.

Tip

Remember that you cannot ignore the volume of water in a gas volume calculation if the temperature is above 100 °C and the water is in the gaseous state.

Example

What volume of oxygen reacts with 60 cm^3 methane and what volume of carbon dioxide is produced if all volumes are measured at the same temperature and pressure?

Notes on the method

Write the balanced equation.

Note that below 100 °C the water formed condenses to an insignificant volume of liquid.

Apply the rule that the ratios of gas volumes are the same as the ratio of the amounts in moles if measured under the same conditions of temperature and pressure.

Answer

The equation for the reaction is:

$$CH_4(g) \quad + \quad 2O_2(g) \quad \rightarrow \quad CO_2(g) + 2H_2O(l)$$

1 mol   2 mol   1 mol
1 volume   2 volumes   1 volume

So, 60 cm^3 methane reacts with 120 cm^3 oxygen to produce 60 cm^3 carbon dioxide.

The other approach to gas volume calculations is also based on the fact that the volume of a gas, under given conditions, depends only on the amount of gas in moles. It is possible to determine the molar volume of a gas given the equation for a reaction that forms the gas.

Core practical 1

Measuring the molar volume of a gas

A group of students carried out an experiment to find the volume of hydrogen produced when magnesium reacts with excess dilute hydrochloric acid. One of the students drew the diagram in Figure 5.6 to describe the method used. Each student used a different, measured, length of ribbon.

Results

The results are shown in Table 5.3.

Mass of 25.0 cm of clean magnesium ribbon = 0.200 g

Questions

1. Explain the apparatus and technique used by the students to start the reaction and collect the gas given off.
2. Plot a graph of the volume of gas given off against the length of magnesium ribbon used. Draw a line of best fit.
3. Calculate the length of magnesium ribbon that gives 1.0×10^{-3} mol of the metal.
4. Read off from the line on the graph the volume of gas formed when 1.0×10^{-3} mol metal reacts with excess dilute hydrochloric acid.
5. Write the equation for the reaction of magnesium with hydrochloric acid.
6. According to the equation, how much hydrogen, in moles, is formed when 1.0×10^{-3} mol magnesium reacts?
7. Use the results to calculate the molar volume of hydrogen.
8. How can the ideal gas equation be used to evaluate the accuracy of the experiment? What other measurements would be needed?
9. Suggest likely sources of measurement uncertainty that might have affected the results.

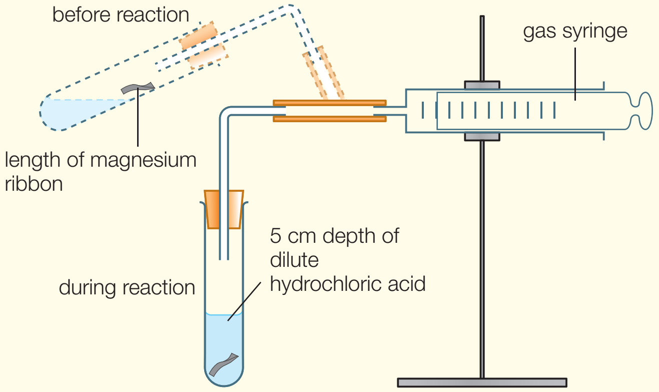

before reaction
gas syringe
length of magnesium ribbon
5 cm depth of dilute hydrochloric acid
during reaction

Figure 5.6 Apparatus for measuring the volume of gas formed when a metal reacts with an acid.

Table 5.3

Length of magnesium ribbon/cm	Volume of hydrogen gas collected/cm^3
1.0	7.5
2.0	16.5
3.0	24.5
4.0	31.0
5.0	39.5
6.0	47.5

Tip

Refer to Practical skills sheets 1, 3, 4 and 5, which you can access using the QR code for Chapter 5 on page 313.

Test yourself

15 Assuming that all gas volumes are measured under the same conditions of temperature and pressure, what volume of oxygen is needed to react with 50 cm^3 ethane, C_2H_6, when it burns, and what volume of carbon dioxide forms?

16 What volume of gas forms at room temperature and pressure when 0.654 g of zinc reacts with excess dilute hydrochloric acid?

5.5 Amounts in solutions

The **concentration** of a solution shows how much solute is dissolved in a certain volume of solution. It can be measured in grams per cubic decimetre ($g\,dm^{-3}$) but in chemistry it is more useful to measure concentrations in moles per cubic decimetre ($mol\,dm^{-3}$). For example, a solution of sodium hydroxide containing 1.0 $mol\,dm^{-3}$ has one mole of sodium hydroxide (40.0 g of NaOH) in 1.0 dm^3 (1000 cm^3) of solution.

Key terms

Concentration/$g\,dm^{-3}$ $= \dfrac{\text{mass of solute/g}}{\text{volume of solution/dm}^3}$

Concentration/$mol\,dm^{-3}$ $= \dfrac{\text{amount of solute/mol}}{\text{volume of solution/dm}^3}$

Tip

Concentrations are measured in moles per dm^3 of solution – not per dm^3 of water used to make up the solution. This is because there are small volume changes when solutes dissolve in water.

Example

A car battery contains 2350 g of sulfuric acid (H_2SO_4) in 6.0 dm^3 of the battery liquid. What is the concentration of sulfuric acid in:

a) $g\,dm^{-3}$ **b)** $mol\,dm^{-3}$?

Notes on the method

Divide the mass in grams of solute by the volume in dm^3 to find the concentration in $g\,dm^{-3}$.

Divide the mass of solute by its molar mass to find its amount in moles.

Divide the amount in moles of solute by the volume in dm^3 to find the concentration in $mol\,dm^{-3}$.

Answer

a) Concentration of the acid/$g\,dm^{-3}$ $= \dfrac{\text{mass of solute/g}}{\text{volume of solution/dm}^3}$

$$= \frac{2350\,g}{6.0\,dm^3}$$

$$= 392\,g\,dm^{-3}$$

b) $M(H_2SO_4) = 98.1\,g\,mol^{-1}$

So, amount of H_2SO_4 in the battery $= \dfrac{2350\,g}{98.1\,g\,mol^{-1}} = 24.0\,mol$

$$\text{Concentration} = \frac{\text{amount of solute/mol}}{\text{volume of solution/dm}^3} = \frac{24.0\,mol}{6.0\,dm^3}$$

$$= 4.0\,mol\,dm^{-3}$$

When ionic compounds dissolve, the ions separate in the solution.

For example:

$$CaCl_2(s) \xrightarrow{aq} Ca^{2+}(aq) + 2Cl^-(aq)$$

So, if the concentration of $CaCl_2$ is 0.1 $mol\,dm^{-3}$, then the concentration of Ca^{2+} is also 0.1 $mol\,dm^{-3}$, but the concentration of Cl^- is 0.2 $mol\,dm^{-3}$.

Test yourself

17 What is the concentration, in mol dm^{-3}, of a solution containing:

- **a)** 4.25 g silver nitrate, $AgNO_3$, in 500 cm^3 solution
- **b)** 4.0 g sodium hydroxide, NaOH, in 250 cm^3 of solution
- **c)** 20.75 g potassium iodide, KI, in 200 cm^3 of solution?

18 What mass of solute is present in:

- **a)** 50 cm^3 of 2.0 mol dm^{-3} sulfuric acid
- **b)** 100 cm^3 of 0.010 mol dm^{-3} potassium manganate(VII), $KMnO_4$
- **c)** 250 cm^3 of 0.20 mol dm^{-3} sodium carbonate, Na_2CO_3?

5.6 Solutions for quantitative analysis

Quantitative analysis involves techniques which answer the question 'How much?' In many laboratories, quantitative analysis is based on instrumental techniques such as chromatography and spectroscopy (see Chapter 7).

Accurate chemical analysis generally involves preparing a solution of an unknown sample. It may then be necessary to dilute the solution before analysing it by **titration** or by some instrumental method. Titrations are an important procedure for checking and calibrating instrumental methods. In a titration, the analyst finds the volume of the sample solution that reacts with a certain volume of a reference solution with an accurately known concentration. Titrations are widely used because they are quick, convenient, accurate and easy to automate.

Key term

A **titration** is a volumetric analysis technique for finding the concentrations of solutions and for investigating the amounts of chemicals involved in reactions.

Many laboratories have automatic instruments for carrying out titrations (Figure 5.7), but the principle is exactly the same as in titrations where the volumes are measured with a traditional burette and pipette. Volumetric titrations with the kinds of glassware used in school and college laboratories are widely used in the food, pharmaceutical and other industries.

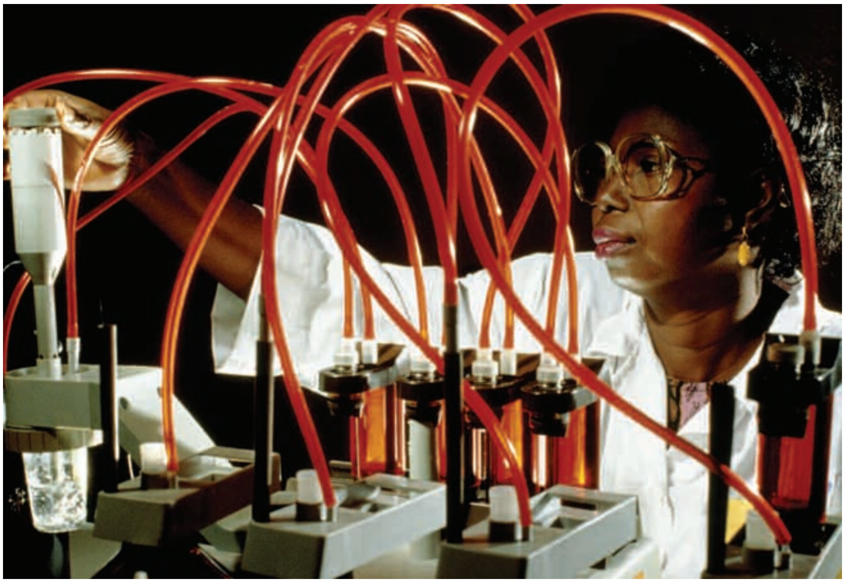


Figure 5.7 A scientist in Nigeria adjusting an automatic titration device. This is being used to check that a pharmaceutical product contains the right amount of folic acid.

Test yourself

19 Why might the results of the following examples of quantitative analysis be important and why must the results be accurate:

a) the concentration of sugars in urine

b) the concentration of alcohol in blood

c) the percentage by mass of haematite (iron ore) in a rock sample

d) the concentration of nitrogen oxides in the air?

Pipettes, burettes and graduated flasks make it possible to measure out volumes of solutions very precisely during a titration. There are correct techniques for using all this glassware which must be followed carefully for accurate results.

Standard solutions

Any titration involves two solutions. Typically, a measured volume of one solution is run into a flask from a pipette. Then the second solution is added, bit by bit, from a burette until the colour change of an indicator, or the change in a signal from an instrument, shows that the reaction is complete. The procedure only gives accurate results if the reaction between the two solutions is rapid and proceeds exactly as described by the chemical equation. So long as these conditions apply, titrations can be used to study acid–base and other types of reactions.

Standard solutions make volumetric analysis possible. The direct way of preparing a standard solution is to dissolve a known mass of a chemical in water and then to make the volume of solution up to a definite volume in a graduated flask.

This method for preparing a standard solution is only appropriate with a chemical that:

- is very pure
- does not gain or lose mass when in the air
- has a relatively high molar mass so that weighing errors are minimised.

Chemicals that meet these criteria are called **primary standards**. A titration with a primary standard can be used to measure the concentration of a solution.

Key terms

A **standard solution** is a solution with an accurately known concentration.

A **primary standard** is a chemical which can be weighed out accurately to make up a standard solution.

Test yourself

20 Suggest a reason why sodium hydroxide cannot be used as a primary standard (see Figure 4.9).

21 Suggest a reason why anhydrous sodium carbonate can be used as a primary standard but hydrated sodium carbonate cannot.

Core practical 2

Preparation of a standard solution from a solid acid

A standard solution of a solid acid was prepared in a graduated flask using the procedure illustrated in Figure 5.8. The acid used was a potassium salt of benzene-1,2-dicarboxylic acid. The traditional name for the salt is potassium hydrogenphthalate, which is often referred to as KHP.

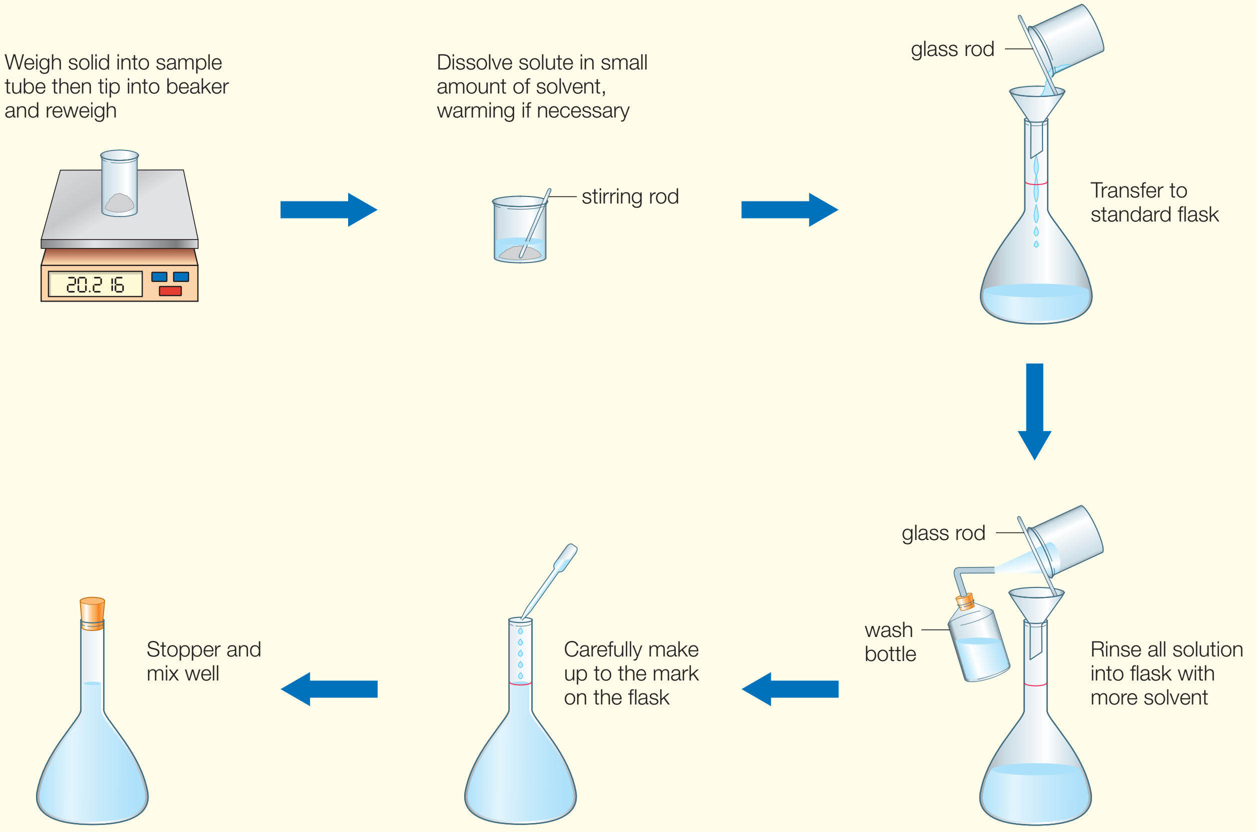

Weigh solid into sample tube then tip into beaker and reweigh
20.216
Dissolve solute in small amount of solvent, warming if necessary
stirring rod
glass rod
Transfer to standard flask
glass rod
wash bottle
Rinse all solution into flask with more solvent
Carefully make up to the mark on the flask
Stopper and mix well

Figure 5.8 Using a standard flask to prepare a solution with a specified concentration.

1 The formula of KHP is $KHC_8H_4O_4$. What mass of KHP is needed to prepare a 0.10 mol dm^{-3} solution in a 250 cm^3 graduated flask?

2 Suggest a reason why KHP is a better primary standard to use than the oxalic acid ($H_2C_2O_4.2H_2O$) which is also available as a pure solid.

3 **a)** Why is the solution poured down a glass rod as the liquids are transferred from the beaker to the graduated flask?

b) What other steps must be taken to ensure that every drop of the solution is transferred to the graduated flask?

4 After transferring the solution from the beaker, the graduated flask is filled with water to within about 1 cm of the graduation mark. The contents are then mixed well before finally adding water dropwise until the meniscus just rests on the mark. What are the reasons for following this procedure?

5 Calculate the concentration of the standard solution made by the procedure in Figure 5.8 when the readings from the balance when weighing out the solid are as follows and the volume of the graduated flask is 250.0 cm^3.

Mass of weighing bottle plus sample of KHP = 20.216 g

Mass of weighing bottle after tipping KHP into the beaker = 14.855 g

Diluting a solution quantitatively

Quantitative dilution is an important procedure in analysis. Two common reasons for carrying out dilutions are:

- to make a solution with the concentration needed for a particular experiment from a standard solution
- to dilute an unknown sample for analysis to give a concentration suitable for titration.

The procedure for dilution is to take a measured volume of the more concentrated solution with a pipette (or burette) and run it into a graduated flask. The flask is then carefully filled to the mark with pure water.

The key to calculating the volumes to use when diluting a solution is to remember that the amount, in moles, of the chemical dissolved in the diluted solution is equal to the amount, in moles, of the chemical taken from the concentrated solution. If c is the concentration in $\mathrm{mol\,dm^{-3}}$ and V is the volume in $\mathrm{dm^3}$, then we can write the following expressions.

The amount, in moles, of the chemical taken from the concentrated solution = $c_A V_A$

The amount, in moles, of the same chemical in the diluted solution = $c_B V_B$

These two amounts are the same, so $c_A V_A = c_B V_B$

Example

An analyst requires a $0.10\,\mathrm{mol\,dm^{-3}}$ solution of sodium hydroxide, NaOH(aq). The analyst has a $250\,\mathrm{cm^3}$ graduated flask and a supply of $0.50\,\mathrm{mol\,dm^{-3}}$ sodium hydroxide solution. What volume of the concentrated solution should be measured into the graduated flask?

Notes on the method

Use the relationship $c_A V_A = c_B V_B$

This can be rearranged to show that: $V_A = \dfrac{c_B V_B}{c_A}$

Answer

$c_A = 0.50\,\mathrm{mol\,dm^{-3}}$ $\quad$ $c_B = 0.10\,\mathrm{mol\,dm^{-3}}$

V_A = to be calculated $\quad$ $V_B = 250\,\mathrm{cm^3} = 0.25\,\mathrm{dm^3}$

$$V_A = \frac{c_B V_B}{c_A} = \frac{0.10\,\mathrm{mol\,dm^{-3}} \times 0.25\,\mathrm{dm^3}}{0.50\,\mathrm{mol\,dm^{-3}}}$$

$$= 0.050\,\mathrm{dm^3} = 50.0\,\mathrm{cm^3}$$

Pipetting $50.0\,\mathrm{cm^3}$ of the concentrated solution into the $250\,\mathrm{cm^3}$ graduated flask and making up to the mark with pure water gives the required dilution after thorough mixing.

Test yourself

22 How would you prepare:

- **a)** a 0.0500 mol dm^{-3} solution of HCl(aq) given a 1000 cm^3 graduated flask and a 1.00 mol dm^{-3} solution of the acid
- **b)** a 0.010 mol dm^{-3} solution of NaOH(aq) given a 500 cm^3 graduated flask and a 0.50 mol dm^{-3} solution of the alkali?

23 What is the concentration of the solution produced when making up to the mark with pure water and mixing:

- **a)** 10.0 cm^3 of a 0.010 mol dm^{-3} solution of $AgNO_3$(aq) in a 100 cm^3 graduated flask
- **b)** 50.0 cm^3 of a 2.00 mol dm^{-3} solution of nitric acid in a 250 cm^3 graduated flask?

5.7 Titration principles

A titration involves two solutions. A measured volume of one solution is run into a flask. The second solution is then added, bit by bit, from a burette until the reaction is complete (Figure 5.9).

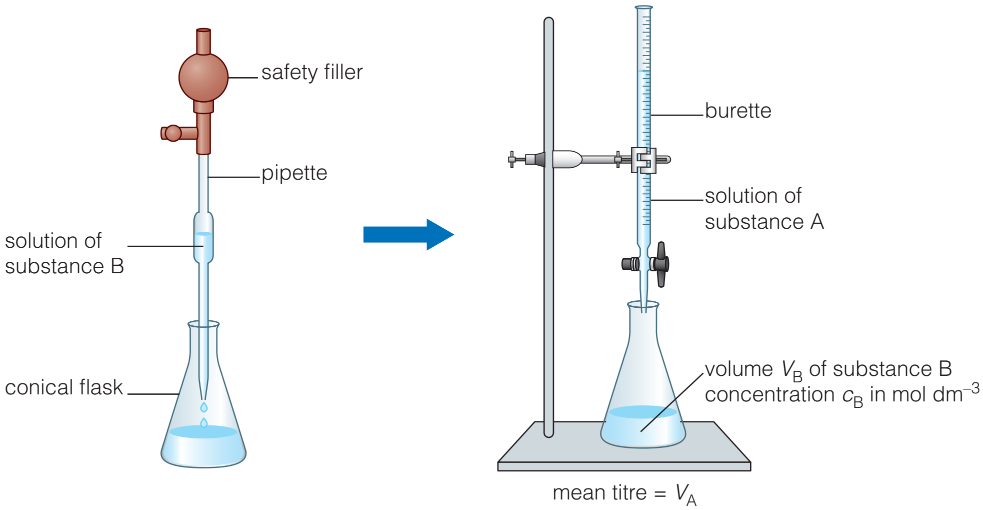

safety filler
pipette
solution of substance B
conical flask
burette
solution of substance A
volume V_B of substance B concentration c_B in mol dm^{-3}
mean titre = V_A

Figure 5.9 The apparatus used for a titration based on a reaction between two chemicals in solution, A and B.

Some titrations are used to investigate reactions. In these experiments the concentrations of both solutions are known and the aim is to determine the equation for the reaction.

More often, titrations are used to measure the concentration of an unknown solution, knowing the equation for the reaction and using a second solution of known concentration.

In general, n_A moles of A react with n_B moles of B.

$$n_A A + n_B B \rightarrow \text{products}$$

The concentration of solution B in the flask is c_B and the concentration of solution A in the burette is c_A. Both are measured in mol dm^{-3}. The analyst uses

Key terms

The **end-point** in a titration is the point at which a colour change shows that enough of the solution in the burette has been added to react with the chemical in the flask.

The **equivalence point** during a titration is reached when the amount of reactant added from a burette is just enough to react exactly with all the measured amount of chemical in the flask.

Tip

Instead of trying to remember a formula for working out titration calculations, it is better to work through the calculation, step by step, as shown in the example in Section 5.8.

a pipette to run a volume V_B of solution B into the flask. Then solution A is added from the burette until an indicator shows that the reaction is complete. This is the **end-point** of the titration.

In a well planned titration the colour change observed at the end-point corresponds exactly with the point when the amount in moles of the reactant added from a burette is just enough to react exactly with all of the measured amount of chemical in the flask as shown by the balanced equation. This is the **equivalence point**.

At the end-point, the volume added is the titre, V_A. The analyst should repeat the titration enough times to achieve consistent results.

Titration calculations

In the laboratory, volumes of solutions are normally measured in cm^3, but they should be converted to dm^3 in calculations so that they are consistent with the units used for concentrations.

The amount, in moles, of B in the flask at the start = $c_B \times V_B$

The amount, in moles, of A added from the burette = $c_A \times V_A$

The ratio of these amounts must be the same as the ratio of the reacting amounts n_A and n_B. This means that:

$$\frac{c_A \times V_A}{c_B \times V_B} = \frac{n_A}{n_B}$$

In any titration, all but one of the values in this relationship are known. The one unknown is calculated from the results, so this formula can be used to analyse titration results. It is generally better, however, to work out the results, step by step, as shown in the worked examples in this chapter.

Analysing solutions

In titrations designed to analyse solutions, the equation for the reaction is given so that the ratio n_A/n_B is known. The concentration of one of the solutions is also known. The volumes V_A and V_B are measured during the titration. Substituting all the known quantities in the titration formula allows the concentration of the unknown solution to be calculated.

Investigating reactions

In titrations to investigate reactions, the problem is to determine the ratio n_A/n_B. The concentrations c_A and c_B are known and the volumes V_A and V_B are measured during the titration. So the ratio n_A/n_B can be calculated from the formula.

5.8 Acid–base titrations

Coloured indicators can be used to detect the end-points of acid–base reactions. These are chemicals which change colour as the pH varies. Typically, an indicator completes its colour change over a range of about two pH units as shown in Table 5.4. In any acid–base titration, there is a sudden change of pH at the end-point. The chosen indicator must, therefore, complete its colour change within the range of pH values spanned at the end-point.

Some acids and alkalis are fully ionised in solution. These are **strong acids** and strong alkalis. For a titration of a strong acid with a strong alkali, the pH jumps from around pH 3 to pH 10 at the end-point. Most common indicators change colour sharply within this range.

Other acids are only slightly ionised in solution. These are **weak acids**. During a titration of a weak acid with a strong alkali, the jump is from about pH 6 to pH 10. So the indicator must be chosen with care so that it changes colour in this range.

Table 5.4 Some common indicators and the pH range over which they change colour.

Indicator	Colour change low pH–high pH	pH range over which the colour change occurs
Methyl orange	Red–yellow	3.2–4.2
Methyl red	Yellow–red	4.8–6.0
Bromothymol blue	Yellow–blue	6.0–7.6
Phenolphthalein	Colourless–red	8.2–10.0

Key terms

A **strong acid** is one that is fully ionised when it dissolves in water. Hydrochloric acid is an example of a strong acid.

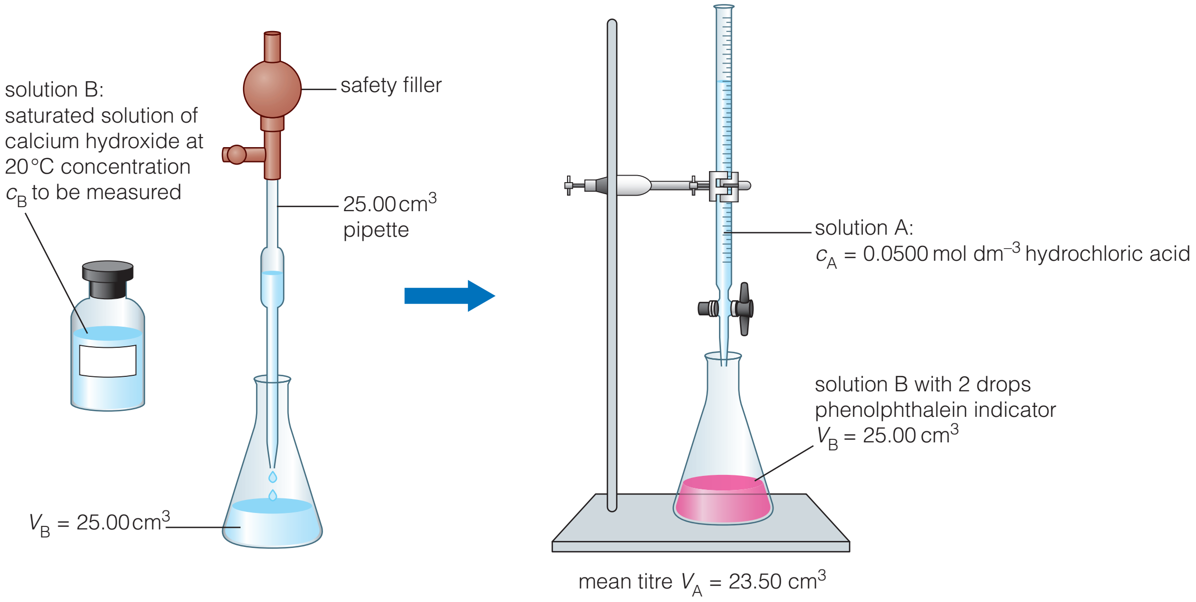
A **weak acid** is one that is only slightly ionised when it dissolves in water. Ethanoic acid is an example of a weak acid.

Tip

You will learn more about indicators and why they change colour over different pH ranges later in your Advanced chemistry course.

Example

Calcium hydroxide is an alkali that is only slightly soluble in water. Its solubility, at a given temperature, can be determined by titration of a saturated solution of the alkali with a standard solution of hydrochloric acid, as shown in Figure 5.10. Work out the solubility of $Ca(OH)_2$ in moles per dm^3, and in grams per dm^3, given that the volume V_A of acid added from the burette at the end-point was $23.50\,cm^3$.



solution B: saturated solution of calcium hydroxide at 20 °C concentration c_B to be measured
safety filler
$25.00\,cm^3$ pipette
$V_B = 25.00\,cm^3$
solution A: $c_A = 0.0500\,mol\,dm^{-3}$ hydrochloric acid
solution B with 2 drops phenolphthalein indicator $V_B = 25.00\,cm^3$
mean titre $V_A = 23.50\,cm^3$

Figure 5.10 A titration to determine the solubility of calcium hydroxide.

Notes on the method

Both the volume and concentration of the acid are known, so the first step is to work out the amount in moles of acid added from the burette.

Next look at the balanced equation to see how much $Ca(OH)_2$ this amount of acid reacts with.

Finally work out the concentration of calcium hydroxide in the saturated solution.

Answer

Step 1: Work out the amount of acid added from the burette.
The concentration of the acid, $c_A = 0.0500\,\text{mol dm}^{-3}$

$$\text{Amount of HCl(aq) added from the burette} = \frac{23.50}{1000}\,\text{dm}^3 \times 0.0500\,\text{mol dm}^{-3}$$
$$= 0.001\,175\,\text{mol}$$

Step 2: Use the equation for the titration reaction to find the amount of alkali in the flask.

$$Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$$

So 1 mol of the alkali reacts with 2 mol of the acid.

Hence the amount of calcium hydroxide in the flask = 0.5 × 0.001 175 mol = 0.0 005 875 mol

Step 3: Work out the concentration of the saturated solution.
The 0.0 005 875 mol of alkali is dissolved in 25.0 cm^3 of saturated solution.
So the concentration of saturated calcium hydroxide solution

$$= 0.0\,005\,875\,\text{mol} \div 0.0250\,\text{dm}^3 = 0.0235\,\text{mol dm}^{-3}$$

The molar mass of calcium hydroxide is 74.1 g mol^{-1}.
So the concentration of saturated calcium hydroxide solution

$$= 0.0235\,\text{mol dm}^{-3} \times 74.1\,\text{g mol}^{-1} = 1.74\,\text{g dm}^{-3}$$

Test yourself

24 Suggest why methyl orange is distinctly orange when the pH is 3.7.

25 A 25.0 cm^3 sample of nitric acid was neutralised by 18.0 cm^3 of 0.150 mol dm^{-3} sodium hydroxide solution. Calculate the concentration of the nitric acid.

26 A 2.65 g sample of anhydrous sodium carbonate was dissolved in water and the solution made up to 250 cm^3. In a titration, 25.0 cm^3 of this solution was added to a flask and the end-point was reached after adding 22.5 cm^3 of hydrochloric acid. Calculate the concentration of the hydrochloric acid.

27 A 41.0 g sample of the acid H_3PO_3 was dissolved in water and the volume of solution was made up to 1 dm^3. 20.0 cm^3 of this solution was required to react with 25.0 cm^3 of 0.800 mol dm^{-3} sodium hydroxide solution. What is the equation for the reaction?

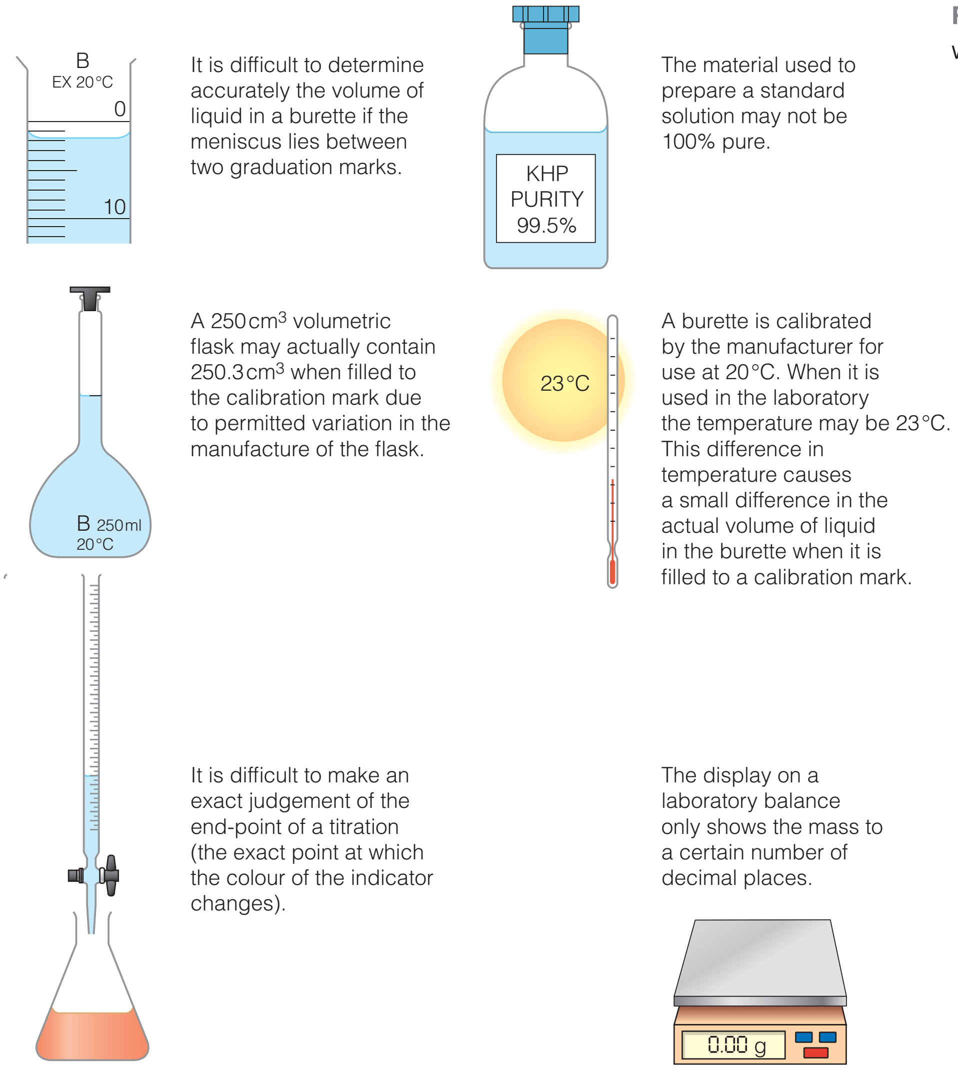
5.9 Evaluating results

Accuracy of data is determined by how close a measured quantity is to the correct value. In chemical analysis the correct value is often not known and so chemists need to estimate the measurement uncertainty.

Every time an analyst carries out a titration, there is some uncertainty in the result. It is important to be able to assess measurement uncertainty (Figure 5.11). Key decisions are based on the results of chemical analysis in healthcare, in the food industry, in law enforcement and in many other areas of life. It is important that the people making these decisions understand the extent to which they can rely on the data from analysis.

Key term

Measurements are **accurate** if they are precise and free from bias.



It is difficult to determine accurately the volume of liquid in a burette if the meniscus lies between two graduation marks.

The material used to prepare a standard solution may not be 100% pure.

A 250 cm^3 volumetric flask may actually contain 250.3 cm^3 when filled to the calibration mark due to permitted variation in the manufacture of the flask.

A burette is calibrated by the manufacturer for use at 20 °C. When it is used in the laboratory the temperature may be 23 °C. This difference in temperature causes a small difference in the actual volume of liquid in the burette when it is filled to a calibration mark.

It is difficult to make an exact judgement of the end-point of a titration (the exact point at which the colour of the indicator changes).

The display on a laboratory balance only shows the mass to a certain number of decimal places.

Figure 5.11 Sources of uncertainty in volumetric analysis.

Random errors in titrations

Every time an analyst carries out a titration, there are small differences in the results. This is not because the analyst has made mistakes but because there are factors that are impossible to control. Unavoidable random errors arise in judging when the bottom of the meniscus is level with the graduation on a pipette, in judging the colour change at the end-point and when taking the reading from a burette scale. If these random errors are small, then the results will be close together – in other words, they are **precise** (Figure 5.12). The precision of a set of results can be judged from the range in a number of repeated titrations.

Systematic errors in titrations

Systematic errors mean that the results differ from the true value by the same amount each time. The measurement is always too high or too low, so it is **biased** in one way or the other (Figure 5.12). One source of systematic error is the tolerance allowed in the manufacture of graduated glassware. The tolerance for grade B 250 cm^3 graduated flasks is ±0.3 cm^3. This means that

Key terms

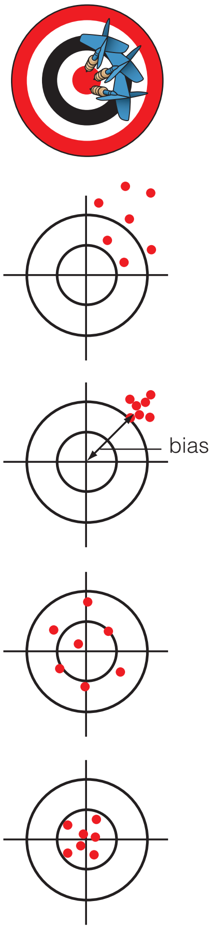
Measurements are **precise** if repeat measurements have values that are close together. Precise measurements have a small random error.

Bias arises from systematic errors which affect all the measurements in the same way, making them all higher or lower than the true value. Systematic errors do not average out.

when an analyst chooses to use a particular flask, the volume of solution may be as little as 249.7 cm^3 or as much as 250.3 cm^3 when it is filled correctly to the graduation mark. This introduces a systematic error when using this same flask to make up solutions for a series of titrations.

Similar tolerances are allowed for pipettes and burettes: for a class B 25 cm^3 pipette the tolerance is ± 0.06 cm^3, while for a class B 50 cm^3 burette the tolerance is ± 0.1 cm^3.

Systematic errors can be allowed for by calibrating the measuring instruments. It is possible to calibrate pipettes and burettes by using them to measure out pure water and then weighing the water with an accurate balance.



A darts player is practising throwing darts at a board. The aim is to get all the darts close together near the centre of the board. The results of some of the attempts are shown below.

1st attempt: The shots are quite widely scattered and some have not even hit the board. The shots show *poor precision* as they are quite widely scattered. There is also a *bias* in where the shots have landed – they are grouped in the top right-hand corner, not near the centre of the board.

2nd attempt: The *precision* has improved as the shots are now more closely grouped. However, there is still a *bias*, as the group of shots is offset from the centre of the board.

3rd attempt: The player has improved to *reduce* the *bias* – all the shots are now on the board and scattered round the centre. Unfortunately the *precision* is *poor* as the shots are quite widely scattered.

Some time later: The shots are *precise* and *unbiased* – they are all grouped close together in the centre of the board.

Figure 5.12 Throwing darts at the bullseye of a dartboard illustrates the notions of precision and bias. Reliable players throw precisely and without bias so that their darts hit the centre of the board accurately.

Tip

Refer to Practical skills sheet 5, 'Identifying errors and estimating uncertainties', to find out how to estimate measurement errors and calculate overall measurement uncertainties.

Test yourself

28 Identify examples of random and systematic error when:

a) using a pipette

b) using a burette

c) making up a standard solution in a graduated flask.

Core practical 3

Finding the concentration of a solution of hydrochloric acid

A student carried out a titration to determine the concentration of a solution of hydrochloric acid. He used the apparatus shown in Figure 5.13 and followed the instructions numbered A–F. The results are shown in Table 5.5.

Tip

Refer to Practical skills sheets 5 and 6, which you can access using the QR code for Chapter 5 on page 312:

5 Identifying errors and estimating uncertainties

6 Measuring chemical amounts by titration.

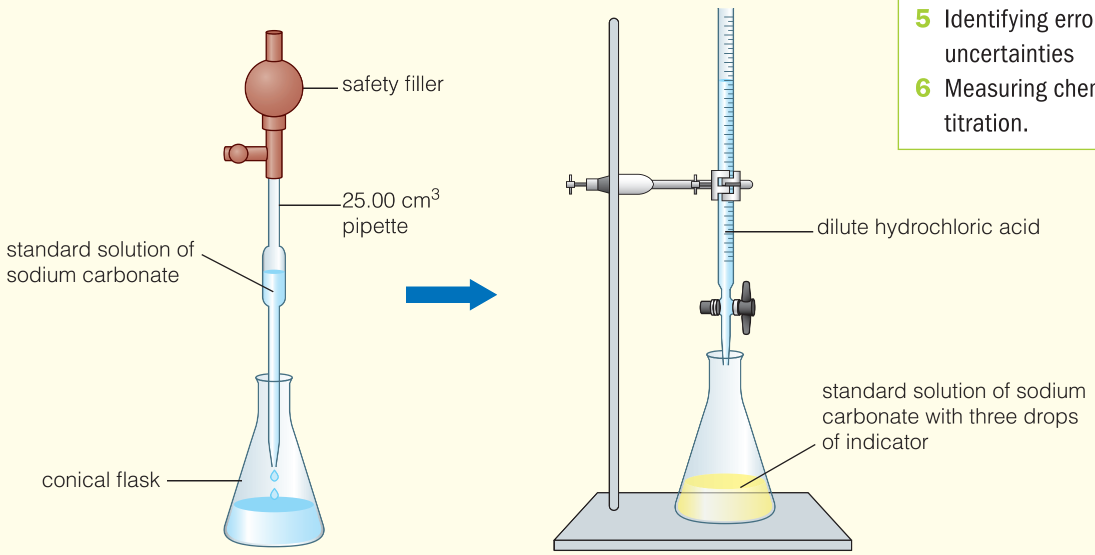

safety filler
25.00 cm³ pipette
standard solution of sodium carbonate
conical flask
dilute hydrochloric acid
standard solution of sodium carbonate with three drops of indicator

Figure 5.13

Instructions

A Wash out the pipette, burette and conical flask with pure (deionised or distilled) water.

B Rinse the burette with a little of the solution of hydrochloric acid, then fill the burette, remembering to run out some of the solution through the tap.

C Rinse the 25.00 cm^3 pipette with the standard solution of sodium carbonate. Fill the pipette to the mark and run out the measured alkali into a clean conical flask, allowing the pipette to drain adequately.

D Add three drops of methyl orange indicator.

E Carry out one rough and then accurate titrations to give two titres that are within 0.10 cm^3 of each other. In the accurate titrations the colour change at the end-point should be caused by adding one drop of acid.

F Each time, record the initial and final burette readings. Take the burette readings to the nearest half-scale division.

1. Explain briefly the reasons for carrying out each of the steps A–F.
2. Describe what the student should do to 'allow the pipette to drain adequately' in step C.
3. The standard solution of sodium carbonate was prepared with 2.920 g anhydrous Na_2CO_3 in a 500 cm^3 graduated flask. Calculate the concentration of the sodium carbonate solution.
4. How should the student read the burette in order to justify recording results to the nearest 0.05 cm^3?
5. Use the titration results in Table 5.5 to calculate the concentration of the dilute hydrochloric acid.
6. The glassware used for the titration was all grade B apparatus. Estimate the total uncertainty in your calculated result.

Results

Burette: Solution of hydrochloric acid to be standardised

Pipette: Standard solution of sodium carbonate

Indicator: Methyl orange

Table 5.5 Titration results.

	Rough	Accurate 1	Accurate 2	Accurate 3
Final burette reading	28.0	24.00	25.70	26.50
Initial burette reading	5.0	1.55	3.30	4.15
Titre/cm³	23.0	22.45	22.40	22.35

5.10 Yields and atom economies

If there are no losses during a chemical reaction, the starting reactants are converted to the required products. Often, some reactants are added in excess to ensure that the most valuable reactant is converted to as much product as possible. Then the reactant that is not in excess is the substance that limits the maximum yield that is possible.

Converting all of the **limiting reagent** to the desired product gives a 100% **yield**. But few reactions are so efficient and many give low yields. There are various reasons why yields are not 100%:

- the reactants may not be totally pure
- some of the product may be lost during transfer of the chemicals from one container to another, when the product is separated and purified
- there may be side reactions in which the reactants form different products
- some of the reactants may not react because the reaction is so slow (Chapter 9) or because it comes to equilibrium (Chapter 10).

Key terms

A **limiting reagent** is a substance which is present in an amount which limits the theoretical yield.

Yield calculations are used to assess the efficiency of a chemical process. The actual yield is the mass of product obtained from a reaction. The theoretical yield is the mass of product obtained if the reaction goes according to the equation.

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Example

A modern gas-fuelled lime kiln produces 500 kg of calcium oxide, CaO (quicklime), from 1000 kg of crushed calcium carbonate, $CaCO_3$(limestone).

What is the percentage yield of calcium oxide? Give your answer to 2 significant figures.

Notes on the method

Start by writing the balanced equation for the reaction.

Use the method for calculating reactant and product masses in Section 5.4.

Answer

The equation for the reaction involved is:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

From the equation, 1 mole $CaCO_3 \rightarrow$ 1 mole CaO

$$[40.1 + 12 + (3 \times 16)]\,\text{g } CaCO_3 \rightarrow (40.1 + 16)\,\text{g } CaO$$

So 100.1 g $CaCO_3 \rightarrow$ 56.1 g CaO

Thus 1 g $CaCO_3 \rightarrow \frac{56.1}{100.1}$ g CaO

$$\text{Theoretical yield from 1000 kg } CaCO_3 = \frac{56.1}{100.1} \times 1000\,\text{kg CaO}$$

$$= 560\,\text{kg}$$

$$\text{The actual yield of CaO} = 500\,\text{kg CaO}$$

$$\text{Percentage yield} = \frac{500\,\text{kg}}{560\,\text{kg}} \times 100 = 89\%$$

Test yourself

29 1000 kg of pure iron(III) oxide, Fe_2O_3, was reduced to iron and 630 kg of iron was obtained. What are the theoretical and percentage yields of iron?

30 500 kg of calcium oxide (quicklime) was reacted with water to produce calcium hydroxide, $Ca(OH)_2$ (slaked lime). 620 kg of calcium hydroxide was produced. Calculate the theoretical and percentage yields.

Atom economy

The yield in a laboratory or industrial process focuses on the desired product. But many atoms in the reactants do not end up in the desired product. This can lead to a huge waste of material. For example, when calcium carbonate (limestone) is decomposed to produce calcium oxide (quicklime), part of the calcium carbonate is lost as carbon dioxide in the atmosphere.

The waste in many reactions has led scientists and industrialists to use the term **atom economy** in calculating the overall efficiency of a chemical process (Figure 5.14). The atom economy of a reaction is the molar mass of the desired product expressed as a percentage of the sum of the molar masses of all the products as shown in the equation for the reaction.

$$\text{atom economy} = \frac{\text{molar mass of the desired product}}{\text{sum of the molar masses of all the products}} \times 100\%$$

Example

Titanium is manufactured by heating titanium(IV) chloride with magnesium. The equation for the reaction at 1200 °C is:

$$TiCl_4(g) + 2Mg(l) \rightarrow Ti(s) + 2MgCl_2(l)$$

What is the atom economy of this process?

Answer

Molar mass of all products = $M(\text{Ti}) + 2M(\text{MgCl}_2)$

$= 47.9\,\text{g}\,\text{mol}^{-1} + 190.6\,\text{g}\,\text{mol}^{-1} = 238.5\,\text{g}\,\text{mol}^{-1}$

Molar mass of desired product = $47.9\,\text{g}\,\text{mol}^{-1}$

Therefore: atom economy = $47.9 \div 238.5 \times 100\% = 20.1\%$

Almost 80% of the reactants are 'wasted' in the manufacture of titanium by the process described above, because magnesium and chlorine atoms are lost as magnesium chloride. If society is to use raw materials as efficiently as possible, chemists must look for high atom economies as well as high percentage yields, particularly in industrial processes.

400 mg
Ibuprofen Tablets
84 TABLETS
Ibuprofen Tablets
400 mg
84 TABLETS

Figure 5.14 The production of ibuprofen is an excellent example of atom economy. Ibuprofen is an important medicine which reduces swelling and pain. In the 1960s, Boots made ibuprofen in five steps with an atom economy of only 40%. When the patent expired, another company developed a new process requiring just two steps with an atom economy of 100%.

Key terms

Atom economy is a measure of how efficiently a chemical reaction converts the atoms in its reactants to atoms in the product. The atom economy for a reaction is calculated from the balanced equation to show the percentage of the mass of the atoms in the reactants that is converted to the desired product.

Test yourself

31 Calculate the atom economy for:

a) the conversion of nitrogen (N_2) to ammonia (NH_3) in the Haber process:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

b) the fermentation of glucose ($C_6H_{12}O_6$) to ethanol (C_2H_5OH)

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

c) the manufacture of tin (Sn) from tinstone (SnO_2)

$$SnO_2(s) + 2C(s) \rightarrow Sn(s) + 2CO(g)$$

5.11 Tests and observations in inorganic chemistry

Formulae and equations are not only used to solve quantitative problems. They are also important in qualitative analysis.

Qualitative analysis answers the question 'What is it?' In Advanced chemistry courses, this question is often answered by careful observation of the changes during test-tube experiments and flame tests. These changes include gases bubbling off, different smells, precipitates forming, solids dissolving, temperatures changing or new colours appearing.

The skill is knowing what to look for. Some visible changes are much more significant than others and a capable analyst can spot the important changes and know what they mean. Good chemists have a 'feel' for the way in which chemicals behave and recognise characteristic patterns of behaviour. With experience they know what to look for when making observations.

Success also depends on good techniques when mixing chemicals, heating mixtures and testing for gases.

In inorganic chemistry most observations can be explained in terms of a number of types of reaction (see also Chapter 3 and Section 4.1).

Ionic precipitation reactions

This type of reaction can be used to test for negative ions (anions). Adding a solution of silver nitrate to a halide produces a precipitate that can be used to distinguish chlorides, bromides and iodides. Adding a soluble barium salt (nitrate or chloride) to a solution of a sulfate produces a white precipitate of insoluble barium sulfate.

Acid–base reactions

Acids and alkalis are commonly used in chemical tests. Dilute hydrochloric acid is a convenient strong acid. Sodium hydroxide solution is often chosen as a strong base.

Adding dilute hydrochloric acid to a carbonate, for example, adds hydrogen ions to the carbonate ions, CO_3^{2-}, turning them into carbonic acid molecules, H_2CO_3, which immediately decompose into carbon dioxide and water.

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$$

Testing with limewater can then identify the gas given off, confirming that the compound tested is a carbonate.

Hydrogencarbonate ions react in a similar way to carbonate ions.

$$H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$$

The strong base, sodium hydroxide, is used to test for ammonium ions in salts such as ammonium chloride, NH_4Cl. Warming an ammonium salt with a solution of sodium hydroxide produces an alkaline gas with a pungent smell. This gas is ammonia, which is formed when hydroxide ions remove hydrogen ions from ammonium ions.

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$$

Redox reactions

Common oxidising agents used in inorganic tests include chlorine, bromine and acidic solutions of iron(III) ions, manganate(VII) ions or dichromate(VI) ions.

Some reagents change colour when oxidised, which makes them useful for detecting oxidising agents. In particular, a colourless solution of iodide ions turns to a yellow–brown colour when oxidised. This can be a very sensitive test if starch is present because starch gives an intense blue–black colour with low concentrations of iodine. This is the basis of using starch–iodide paper to test for chlorine and other oxidising gases. The oxidation of iodide ions by chlorine or bromine is a redox reaction in which one halogen displaces another (Section 4.10).

Common inorganic reducing agents are metals (in the presence of acid or alkali), sulfur dioxide and iron(II) ions.

Some reagents change colour when reduced. In particular, dichromate(VI) ions in acid change from orange to green. This is the basis of a test for sulfur dioxide gas.

Test yourself

32 For each test, identify the type of chemical reaction taking place, name the products and write a balanced equation for the reaction:

a) testing for iodide ions with silver nitrate solution

b) adding dilute hydrochloric acid to magnesium carbonate

c) testing for sulfate ions with barium chloride

d) strongly heating a sample of potassium nitrate

e) using concentrated ammonia solution to detect hydrogen chloride

f) adding chlorine to a solution of potassium bromide

g) warming ammonium chloride with aqueous sodium hydroxide.

Core practical 7 (part 1)

Tip

Analysis of organic unknowns is covered in Core practical 7 (part 2) in Chapter 7.

Analysis of inorganic unknowns

A series of tests was carried out on two unknown inorganic salts labelled X and Y. The tests and observations were recorded as in Table 5.6.

Table 5.6 Tests and observations on two inorganic unknowns.

Test	Observations with compound X	Observations with compound Y
1 Carry out a flame test on the salt	Lilac coloured flame	Lilac coloured flame
2 Heat a sample of the salt first gently and then more strongly. Identify any gases evolved.	Melts to a colourless liquid. It gives off a colourless gas that relights a glowing splint. On strong heating the gas is tinged with purple. In time the liquid turns red.	Melts to a clear liquid but no gas is given off. In time the hot liquid turns red. There are slight traces of a purple vapour. Molten Y resembles the liquid formed on decomposing X.
3 Allow the residue from test 2 to cool, then add a few drops of concentrated sulfuric acid. Warm gently and then more strongly. Identify any gases evolved.	On cooling, the liquid crystallises to a colourless (white) solid. The cold crystals react immediately with concentrated sulfuric acid. There are traces of a fuming, acidic gas. There is a smell of bad eggs. On warming a purple vapour can be seen.	On cooling, the liquid crystallises to a colourless (white) solid. The solid reacts with concentrated sulfuric acid in the same way as the residue after heating X.
4 Make separate aqueous solutions of X and Y. Mix the two solutions and then add dilute sulfuric acid.	Both X and Y dissolve in water. The solutions are colourless. There is no change at first when the solutions are mixed. On adding dilute sulfuric acid the solutions turn dark brown. Specks of a grey solid separate from the solution.	

1 Describe in outline the procedure for carrying out a flame test on an unknown salt.
2 What precautions have to be taken to avoid contamination, and why are they necessary?
3 Describe in outline the procedure for the gas tests mentioned in Table 5.6.
4 What can be deduced from the results of the flame tests in Table 5.6?
5 Suggest explanations for the observations on heating X and Y, including equations for any reactions.
6 What can be deduced from the results of Test 3?
7 Explain the observations in Test 4 and write an equation for the reaction which took place on adding acid.
8 Describe two further tests that could be carried out to confirm the conclusions based on these observations. What are the expected results of these tests?

Tip

Refer to Practical skills sheet 7, ‘Analysing inorganic unknowns’, which you can access via the QR code for Chapter 5 on page 313.

Exam practice questions

1 Balance the following equations:

a) $Cu_2S(s) + O_2(g) \rightarrow CuO(s) + SO_2(g)$ *(1)*

b) $FeS(s) + O_2(g) + SiO_2(s) \rightarrow FeSiO_3(s) + SO_2(g)$ *(3)*

c) $Fe(NO_3)_3(s) \rightarrow Fe_2O_3(s) + NO_2(g) + O_2(g)$ *(3)*

2 a) How many molecules are present in 4.0 g of oxygen, O_2? (O = 16) *(3)*

b) How many ions are present in 9.4 g of potassium oxide, K_2O? (K = 39.1, O = 16.0) (Avogadro constant = $6.02 \times 10^{23}\,mol^{-1}$) *(3)*

3 One cubic decimetre of tap water was found to contain 0.112 mg of iron(III) ions (Fe^{3+}) and 12.40 mg of nitrate ions (NO_3^-).

a) What are these masses of Fe^{3+} and NO_3^- in grams? *(1)*

b) What are the amounts in moles of Fe^{3+} and NO_3^-? *(2)*

c) What are the numbers of Fe^{3+} and NO_3^- ions? *(2)*

4 a) What is the empirical formula of a substance X with this percentage composition: C = 42.9%, H = 2.36%, N = 16.7% and O = 38.1%? *(4)*

b) Mass spectrometry shows that the relative molecular mass of X is 168. What is the molecular formula of X? *(2)*

5 For each of the following equations, state the type of reaction which it represents.

a) $Ca(NO_3)_2(aq) + K_2CO_3(aq) \rightarrow CaCO_3(s) + 2KNO_3(aq)$

b) $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

c) $2Zn(NO_3)_2(s) \rightarrow 2ZnO(s) + 4NO_2(g) + O_2(g)$

d) $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ *(4)*

6 For each of the following tests, identify the type of chemical reaction taking place, name the products and write a balanced equation for the reaction:

a) testing for iodide ions with silver nitrate solution *(3)*

b) adding dilute hydrochloric acid to magnesium carbonate *(3)*

c) testing for sulfate ions with barium chloride *(3)*

d) heating a sample of zinc carbonate *(3)*

e) adding zinc metal to a solution of copper(II) sulfate. *(3)*

7 The concentration of cholesterol ($C_{27}H_{46}O$) in a patient's blood was found to be $6.0\,mmol\,dm^{-3}$.

a) What is the concentration of cholesterol in $mol\,dm^{-3}$? (1000 mmol = 1 mol) *(1)*

b) Calculate the concentration of cholesterol in $g\,dm^{-3}$. *(2)*

c) What is the mass of cholesterol in $10\,cm^3$ of the patient's blood? *(1)*

8 a) Ammonium sulfate was prepared by adding ammonia solution to $25\,cm^3$ of $2.0\,mol\,dm^{-3}$ sulfuric acid.

$$2NH_3(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

i) What volume of $2.0\,mol\,dm^{-3}$ ammonia solution was needed to just neutralise the sulfuric acid? *(1)*

ii) How can the solution be tested to check that enough ammonia had been added to neutralise all the acid without contaminating the solution? *(2)*

b) Iron(II) sulfate, $FeSO_4$, was dissolved in the solution of ammonium sulfate solution to produce the double salt ammonium iron(II) sulfate hexahydrate, $(NH_4)_2SO_4.FeSO_4.6H_2O$.

i) What mass of iron(II) sulfate was added to the ammonium sulfate solution? *(3)*

ii) The double salt was crystallised from the solution. What mass of ammonium iron(II) sulfate hexahydrate was obtained if the percentage yield was 50%? (H = 1.0, N = 14.0, Fe = 55.8, S = 32.1, O = 16.0) *(4)*

9 a) A compound Z is a compound of carbon, hydrogen and oxygen only. Analysis of a sample of the compound shows that it is made up of 54.5% by mass of carbon and 9.10% by mass of hydrogen. Find the empirical formula of Z. *(4)*

b) When 0.270 g of Z is heated to 100 °C it vaporises to produce $100\,cm^3$ gas at a pressure of 95.0 kPa. Determine the molar mass and molecular formula of Z. *(5)*

10 Excess calcium reacted vigorously with 25.0 cm^3 of 1.00 $mol\,dm^{-3}$ hydrochloric acid producing calcium chloride solution and hydrogen.

a) Write a balanced equation, with state symbols, for the reaction. *(3)*

b) Draw a labelled diagram showing how the hydrogen gas could be collected during the reaction. *(2)*

c) Suggest a procedure for obtaining clean, dry crystals of hydrated calcium chloride, $CaCl_2.6H_2O$, from the solution formed. *(4)*

d) What is the maximum possible yield of hydrated calcium chloride, $CaCl_2.6H_2O$, from the reaction? (Ca = 40.1, H = 1.0, Cl = 35.5, O = 16.0) *(4)*

e) Suggest two reasons why the actual yield of hydrated calcium chloride is much less than the mass calculated in part (d). *(2)*

11 A carbonate of metal M has the formula M_2CO_3. In a titration, a 0.245 g sample of M_2CO_3 was found to neutralise 23.6 cm^3 of 0.150 $mol\,dm^{-3}$ hydrochloric acid. Follow these steps to identify the metal M.

a) Write the equation for the reaction of M_2CO_3 with hydrochloric acid. *(1)*

b) Calculate the amount, in moles, of hydrochloric acid needed to react with the sample of the metal carbonate. *(1)*

c) Use the equation to calculate the amount, in moles, of M_2CO_3 in the sample. *(1)*

d) Use your answer to part (c) and the mass of the sample to calculate the relative formula mass of M_2CO_3. *(2)*

e) Calculate the relative atomic mass of metal M. *(1)*

f) Identify the metal M. *(1)*

12 a) The reaction of ammonia, NH_3, with sodium chlorate(I), NaOCl, produces the rocket fuel hydrazine, N_2H_4, together with sodium chloride and water. Determine the atom economy for the process. *(4)*

b) Calculate the atom economies for each of these processes for making bromoethane:

i) the reaction of ethane, C_2H_6 with bromine to form bromoethane, C_2H_5Br, and hydrogen bromide *(4)*

ii) the reaction of ethene, C_2H_4, with hydrogen bromide to make bromoethane, C_2H_5Br, as the only product. *(3)*

c) Why do both yield and atom economy have to be considered when selecting a process for manufacturing a chemical product? *(6)*

13 a) An analyst investigates an impure sample of sodium sulfate. The impurities are unreactive. A 0.250 g sample of the Na_2SO_4 is dissolved in water. Excess barium chloride is added to the solution to precipitate all the sulfate ions as barium sulfate, $BaSO_4$. The mass of the pure, dry, precipitated barium sulfate is 0.141 g.

Calculate the percentage purity of the sample of sodium sulfate. *(5)*

b) A 0.500 g sample of steel consisting of iron alloyed with carbon and silicon gave off 191 cm^3 hydrogen gas when it reacted with excess hydrochloric acid. The gas volume was measured at room temperature and pressure.

Calculate the percentage of iron in the steel. (Fe = 55.8, molar volume of a gas at room temperature and pressure = 24.0 $dm^3\,mol^{-1}$) *(5)*

14 1.576 g of ethanedioic acid crystals, $(COOH)_2.nH_2O$, was dissolved in water and made up to 250 cm^3. In a titration, 25.0 cm^3 of the acid solution reacted exactly with 15.6 cm^3 of 0.160 $mol\,dm^{-3}$ sodium hydroxide solution.

Show by calculation that this data confirms that $n = 2$ in the formula for the acid. *(8)*

15 A sample of sodium carbonate crystals, $Na_2CO_3.10H_2O$, had lost part of its water of crystallisation on exposure to air. 2.696 g of the crystals were dissolved in water and made up to 250 cm^3 in a graduated flask. In a series of titrations, 20.0 cm^3 portions of the solution were titrated with 0.10 $mol\,dm^{-3}$ hydrochloric acid, giving the results shown in the table.

Titration number	1 (rough)	2	3
Final burette reading/cm^3	22.00	23.00	22.15
Initial burette reading/cm^3	1.00	2.35	1.60

Determine the percentage of loss of mass from the crystals from the titration results. *(10)*

16 Egg shells contain calcium carbonate. It is possible to determine the percentage of calcium carbonate in an egg shell by titration. Calcium carbonate reacts with acids but it is not possible to titrate this directly with an acid from a burette.

An analyst adds 40.00 cm^3 of 1.200 mol dm^{-3} hydrochloric acid (an excess) to a 1.510 g sample of the crushed shell. When the reaction with calcium carbonate in the egg shell is complete, all the solution is transferred to a 250 cm^3 graduated flask. Water is then added to the mark and the diluted solution is well mixed.

Next the analyst titrates separate 25.0 cm^3 portions of the diluted solution with a 0.100 mol dm^{-3} solution of sodium hydroxide to determine the amount of acid that did not react with the egg shell. The mean titre was 24.30 cm^3.

a) Give two reasons why titrating the calcium carbonate in an egg shell with hydrochloric acid from a burette is not possible. *(2)*

b) Use the data about the titration to calculate the amount of excess hydrochloric acid, in moles, left over after reaction with the egg shell. *(3)*

c) Hence calculate how much hydrochloric acid, in moles, reacted with calcium carbonate in the sample of egg shell. *(2)*

d) Use the results to calculate the percentage of calcium carbonate in the egg shell. *(5)*

e) The procedure used in this analysis is called a 'back titration'. Explain what you understand by this term. *(3)*

6.1 Introduction to organic chemistry

6.1.1 Carbon – a special element

Carbon is an amazing element. The number of compounds containing carbon is well over ten million. This is far more than the number of compounds of all the other elements put together. Most compounds containing carbon also contain hydrogen. The main sources of these compounds are organic – living or once-living materials in animals and plants. Because of this, the term 'organic chemistry' is used to describe the branch of chemistry concerned with the study of compounds containing C–H bonds. This covers most of the compounds of carbon. Simple carbon compounds which don't contain C–H bonds, such as carbon dioxide and carbonates, are usually included in the study of inorganic chemistry.

Organic compounds in their millions make up the cells in our bodies, the food we eat, the clothes we wear, the plastic or wooden objects we use and much of the world around us (Figure 6.1.1).

Figure 6.1.1 From the cells in the people's bodies and the fibres in their clothes, to the plastics in the plates and the food on the plates, almost everything in this photo of a summer party consists of organic chemicals.

There are two main reasons why carbon can form so many compounds.

The first reason is that carbon atoms have an exceptional ability to form chains, branched chains and rings of varying size. No other element can form long chains of its atoms in the same way as carbon.

The second reason why carbon can form so many compounds is the relative inertness and unreactive nature of the C–C and C–H bonds, because of their relatively high bond enthalpies (Section 8.7).

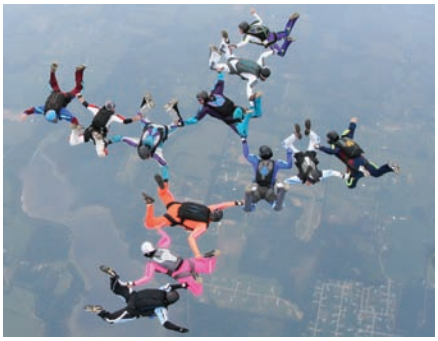


Figure 6.1.2 Sky divers can use their arms and legs to form four links to one another.

Figure 6.1.2 shows sky divers forming four links to each other. Like carbon atoms, they can form chains and rings, although carbon atoms can do it in three dimensions also.

When carbon atoms form a chain or a ring linked by single covalent bonds, no more than two of the bonds on each atom are used. This leaves at least two other bonds on each carbon atom which can bond with other atoms. Carbon often forms bonds with hydrogen, oxygen, nitrogen and halogen atoms (Figure 6.1.3).

A knowledge of organic chemicals enables chemists to extract, synthesise and manufacture a wide range of important products including fuels, plastics, medicines, anaesthetics and antibiotics.

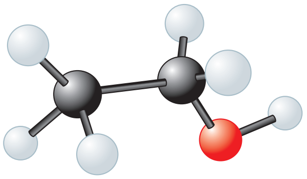


Figure 6.1.3 The structure of ethanol, CH_3CH_2OH. Ethanol is commonly called 'alcohol'. Its structure shows two carbon atoms linked to each other and to hydrogen and oxygen atoms by covalent bonds.

Big molecules

Most molecules in living things are molecules of carbon compounds, so biochemistry and molecular biology are important applications of organic chemistry. The compounds found in living cells include carbohydrates, fats, proteins and nucleic acids. The molecules of these compounds are large – some of them are very large. For example, cellulose, the carbohydrate in cotton, is a natural polymer made of very long chains of glucose units linked together. Its relative molecular mass is about one million.

Organic chemists can synthesise other long-chain molecules by linking together thousands of small molecules to make polymers. These synthetic polymers include polythene (Figure 6.1.4), PVC (polyvinylchloride), polystyrene and nylon.

With so many organic compounds to study and understand, a way of simplifying and organising this knowledge is needed.

Chemists have found a method of classifying organic compounds into families or series, each of which has a distinctive group of atoms called a **functional group** (Section 6.1.2). Examples of these families include **hydrocarbons** such as alkanes and alkenes (Chapter 6.2) and compounds where other elements are also present such halogenoalkanes and alcohols (Chapter 6.3). A family of similar compounds with the same functional group is sometimes called a **homologous series** and can be represented by a **general formula**. For instance, alkanes can be represented by the general formula, C_nH_{2n+2}; alkenes have the general formula C_nH_{2n} and halogenoalkanes containing one halogen atom (X) have the general formula $C_nH_{2n+1}X$.

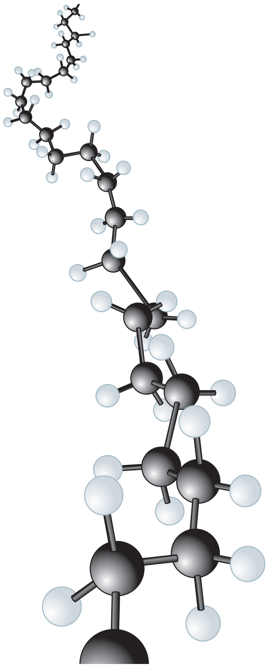


Figure 6.1.4 A short section of a polythene molecule.

Test yourself

1 What is organic chemistry?

2 State two reasons why carbon can form so many compounds.

3 The table shows some mean bond enthalpies. Use the data to answer the following questions.

a) How does the strength of the single C–C bond compare with other single bonds between two atoms of the same non-metal?

b) How does the relative strength of the C–C bond affect the number of carbon compounds?

Bond	Mean bond enthalpy/kJ mol^{-1}
H–H	436
Cl–Cl	243
Br–Br	193
I–I	151
C–C	347
N–N	158
O–O	144

Key terms

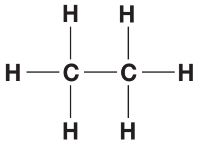
A **functional group** is the group of atoms which gives an organic compound its characteristic properties and reactions.

A **hydrocarbon** is a compound of hydrogen and carbon only.

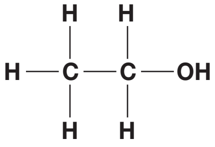
A **homologous series** is a family of compounds which all contain the same functional group and each member of the series contains one $-CH_2-$ unit more than the previous member.

A **general formula** represents all members of a homologous series.

6.1.2 Functional groups



ethane



ethanol

Figure 6.1.5 Structures of ethane and ethanol.

Ethane (CH_3CH_3) and ethanol ($CH_3CH_2{-}OH$) have very different properties despite their similar structures (Figure 6.1.5). Ethane is a gas at room temperature, ethanol is a liquid; ethane does not react with phosphorus(V) chloride, but ethanol reacts vigorously, forming hydrogen chloride gas, which is seen as misty fumes. Clearly, the –OH group in ethanol has a big effect on its properties.

The –OH group in ethanol, called the hydroxyl group, is an example of a functional group – the group of atoms which gives an organic compound its characteristic properties. The functional group in a molecule is responsible for most of its reactions, while the hydrocarbon chain which makes up the rest of the organic compound is relatively unreactive (Figure 6.1.6).

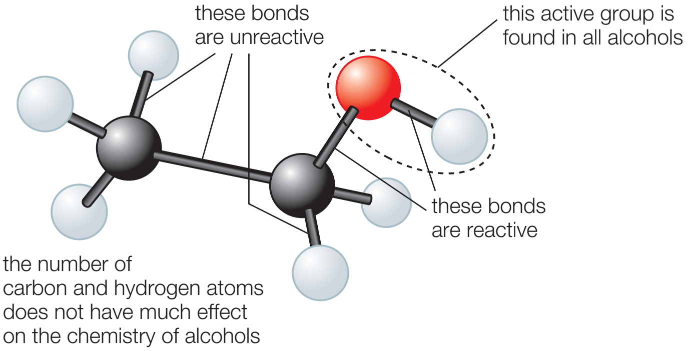


Figure 6.1.6 The structure of ethanol showing the reactive functional group and the unreactive hydrocarbon skeleton.

Tip

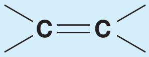
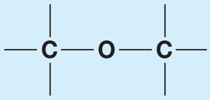
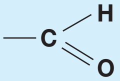
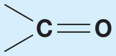
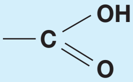
Figure 6.1.6 shows ethanol in its correct three-dimensional representation. The tetrahedral arrangement of bonds around each carbon atom is clear. Figure 6.1.5, however, shows ethanol in a planar (flat) representation. This is much easier to draw, but it is important to remember that the real molecule is not flat and the H–C–H bond angles are not 90° or 180° but are 109.5° (see Section 2.4).

Functional groups, such as –OH, have more or less the same effect whatever the size of the hydrocarbon skeleton to which they are attached.

This makes the study of organic compounds much simpler because all molecules containing the same functional group have similar chemical properties. Their physical properties are similar, but vary depending on the length of the carbon chain attached to the functional group. In this respect, molecules with the same functional group can be regarded as a chemical family like a group of elements in the periodic table.

Ethanol is a member of the series of compounds called alcohols, all of which contain the –OH functional group. Ethene, $CH_2{=}CH_2$, is a member of the series of compounds called alkenes which contain the $>C{=}C<$ functional group. The functional groups and homologous series of organic compounds met in this AS course are shown in Table 6.1.1.

Table 6.1.1 Common functional groups and their series of compounds.

Functional group	Name of the series of compounds	Example
–OH	Alcohols	CH_3CH_2OH ethanol
	Alkenes	$H_2C{=}CH_2$ ethene
$-C\equiv C-$	Alkynes	$HC{\equiv}CH$ ethyne
–Hal	Halogenoalkanes	CH_3CH_2Cl chloroethane
	Ethers	CH_3OCH_3 methoxymethane
 (–CHO)	Aldehydes	CH_3CHO ethanal
	Ketones	CH_3COCH_3 propanone
 (–COOH)	Carboxylic acids	CH_3COOH ethanoic acid
–NH_2	Primary amines	$CH_3CH_2NH_2$ ethylamine

Some organic molecules have two or more functional groups. Lactic acid in sour milk, for example, has both an –OH group and a –COOH group (Figure 6.1.7). In its reactions, lactic acid sometimes acts like an alcohol, sometimes like an acid and sometimes it shows the properties of both types of compound.

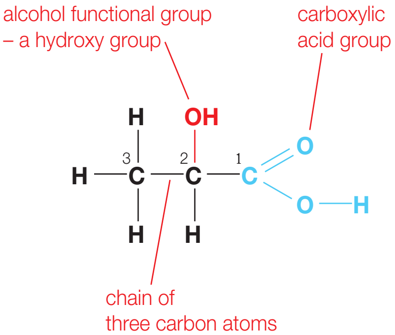


Figure 6.1.7 The structure of lactic acid (2-hydroxypropanoic acid).

Test yourself

4 a) Why do all alkenes have similar chemical properties?

b) Why is there a gradual change in the physical properties of alkenes from gaseous ethene (C_2H_4) to liquid hex-1-ene (C_6H_{12})? (See Section 2.6.)

5 Identify the functional groups in the following compounds and the series to which they belong:

a) $CH_3CH_2CH_2OH$

b) CH_3CH_2CHO

c) CH_3CH_2I

d) $CH_2{=}CHCH_2Cl$.

6 Molecules of amino acids contain the primary amine and the carboxylic acid functional groups. Draw the structure of the amino acid molecule, 2-aminoethanoic acid (common name *glycine*), which contains these two groups bonded to the same carbon atom.

6.1.3 Empirical, molecular and structural formulae

Key term

The **empirical formula** is the simplest whole number ratio of the atoms of each element in a compound.

Empirical formulae

The term 'empirical formula' was introduced in Section 5.2. The **empirical formula** of a compound is the formula found by experiment. In Section 5.2, we used the combined masses of elements in a compound to calculate its empirical formula. The formulae we obtain by this method show the simplest whole number ratio of the atoms of different elements in a compound.

Example

0.150 g of a liquid was analysed and found to contain 0.060 g of carbon, 0.010 g of hydrogen and 0.080 g of oxygen. What is the empirical formula of the liquid?

Notes on the method

The molar masses of the elements come from a table of data.

Convert the masses in grams to amounts in moles by dividing by the molar masses of the atoms of the elements.

Divide the amounts by the smallest of the amounts to find the simplest whole number ratio.

Answer

	C	H	O
Masses of elements combined/g	0.060	0.010	0.080
Molar masses/g mol^{-1}	12.0	1.0	16.0
Amounts of elements combined	$\frac{0.060\,g}{12.0\,g\,mol^{-1}}$	$\frac{0.010\,g}{1.0\,g\,mol^{-1}}$	$\frac{0.080\,g}{16.0\,g\,mol^{-1}}$
Ratio of moles of elements	= 0.005 mol	= 0.010 mol	= 0.005 mol
Simplest whole number ratio	1	2	1

So, the empirical formula of the compound is CH_2O. This empirical formula can represent many different compounds. Three possibilities are shown in Figure 6.1.8.

GLUCOSE C
454g
SAINSBURY'S
MALT
VINEGAR

Figure 6.1.8 Many compounds have the empirical formula CH_2O. These include ethanoic acid (in vinegar) with molecular formula $C_2H_4O_2$, lactic acid (in milk or athletes' muscles) with molecular formula $C_3H_6O_3$ and glucose (in sugar/glucose tablets) with molecular formula $C_6H_{12}O_6$.

Key term

The **molecular formula** gives the actual number of atoms of each element in a molecule.

Molecular formulae

The **molecular formula** of a compound shows the actual number of atoms of each element in one molecule. The molecular formula of ammonia is NH_3 and that of ethanol is C_2H_6O. The term 'molecular formula' only applies to substances that consist of molecules.

For molecular compounds, the relative molecular mass shows whether or not the molecular formula is the same as the empirical formula. A molecular formula is always a simple multiple of the empirical formula.

For example, analysis shows that the empirical formula of octane in petrol is C_4H_9, but the mass spectrum of octane shows that its relative molecular mass is 114.

The relative mass of the empirical formula is given by:

$$\begin{aligned} M_r(C_4H_9) &= (4 \times 12.0) + (9 \times 1.0) \\ &= 57.0 \end{aligned}$$

The relative molecular mass is twice this value – so, the molecular formula is twice the empirical formula.

$\therefore$ the molecular formula of octane = C_8H_{18}

Although the empirical and molecular formulae of organic compounds can be determined by analysis in the way shown above, the modern way to find molecular formulae is by mass spectrometry (Section 7.1).

Test yourself

7 A compound containing only carbon, hydrogen and oxygen was analysed. It consisted of 38.7% carbon and 9.68% hydrogen by mass.

- **a)** What percentage by mass of oxygen does it contain?
- **b)** What is its empirical formula?
- **c)** The relative molecular mass of the compound is 62. What is its molecular formula?

8 A sample of a hydrocarbon was burned completely in oxygen. All the carbon in the sample was converted to 1.69 g of carbon dioxide, and all the hydrogen was converted to 0.346 g of water.

- **a)** What is the percentage of carbon in carbon dioxide?
- **b)** What is the mass of carbon in 1.69 g of carbon dioxide?
- **c)** What is the percentage of hydrogen in water?
- **d)** What is the mass of hydrogen in 0.346 g of water?
- **e)** Use the masses of carbon and hydrogen from parts (b) and (d) to calculate the empirical formula of the hydrocarbon.
- **f)** The relative molecular mass of the hydrocarbon is found to be 26. Deduce its molecular formula.

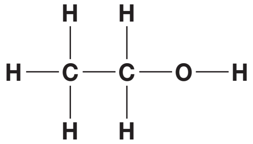
9 A hydrocarbon which consists of 82.8% by mass of carbon has an approximate relative molecular mass of 55.

- **a)** What is its empirical formula?
- **b)** What is its molecular formula?

10 The three compounds shown in Figure 6.1.8 all have the empirical formula CH_2O. Explain how it is possible for different compounds to have the same empirical formula.

Structural formulae

The molecular formula of a compound gives the numbers of atoms of each element in one molecule, but it does not show how the atoms are arranged. To understand the properties of a compound, we need to know its structural formula – this shows which atoms, or groups of atoms, are attached to each other. For example, the molecular formula of ethanol is C_2H_6O – but this does not show how the two carbon atoms, six hydrogen atoms and one oxygen atom are arranged. Its **structural formula**, however, is written as CH_3CH_2OH. This shows that ethanol has a CH_3 group attached to a CH_2 group which, in turn, is attached to an OH group.



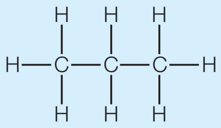
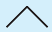
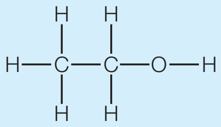
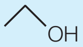
$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H}$

Figure 6.1.9 The displayed formula of ethanol.

Often, it is clearer to draw a full structural formula showing all the atoms and all the bonds (Figure 6.1.9). This type of formula is called a **displayed formula**.

Sometimes a **skeletal formula** is used – this shows only the carbon–carbon bonds and functional groups in a compound (Table 6.1.2).

Table 6.1.2 Alternative formulae for propane and ethanol.

Molecular formula	Structural formula	Displayed formula	Skeletal formula
C_3H_8	$CH_3CH_2CH_3$	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$	
C_2H_6O	CH_3CH_2OH	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H}$	

Skeletal formulae are outline formulae only – they provide a useful shorthand for large and complex molecules. However, skeletal formulae need careful study because they show the hydrocarbon part of a molecule as nothing more than lines for the bonds between carbon atoms and for the bonds from carbon atoms to functional groups. The symbols for carbon and hydrogen atoms in the carbon skeleton are omitted. In contrast, functional groups are shown in full.

Tip

Molecular formulae should not normally be used for describing a particular compound because several different structures may be represented by the same molecular formula. Displayed formulae are clear and unambiguous, but can be time-consuming to draw. Skeletal formulae are the simplest to draw and, with experience, may be the formula of choice, but initially structural formulae should be used as these are clear, unambiguous and easy to understand.

Key terms

A **structural formula** shows in minimal detail which atoms, or groups of atoms, are attached to each other in one molecule of a compound.

A **displayed formula** shows all the atoms and all the bonds between them in one molecule of a compound.

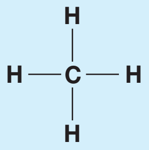
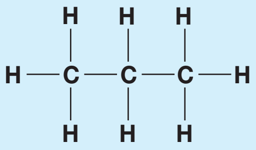
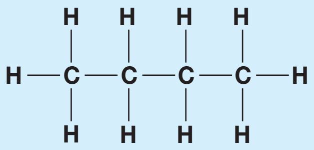
A **skeletal formula** shows the functional groups fully, but the hydrocarbon part of a molecule simply as lines between carbon atoms, omitting the symbols for carbon and hydrogen atoms.

Activity

The alkanes – an important series of organic compounds

Methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) are the first four members of the homologous series of alkanes. Most of their empirical, molecular, structural and displayed formulae are shown in Table 6.1.3.

Table 6.1.3 Empirical, molecular, structural and displayed formulae of the first four alkanes.

Name	Methane	Ethane	Propane	Butane
Empirical formula	CH_4		C_3H_8	C_2H_5
Molecular formula	CH_4	C_2H_6		C_4H_{10}
Structural formula		CH_3CH_3	$CH_3CH_2CH_3$	
Displayed formula				

1 Copy and complete the table by adding the missing formulae.

2 The names of all alkanes end in -ane. The names of the first four alkanes in Table 6.1.3 do not follow a logical system. All other straight-chain alkanes are named using a Greek numerical prefix for the number of carbon atoms in one molecule, with the ending -ane. So, C_5H_{12} is pentane and C_7H_{16} is heptane. The prefixes are the same as those used for geometrical figures (pentagon, etc.).

What is the name for:

a) $CH_3CH_2CH_2CH_2CH_2CH_3$

b) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$?

3 Which of the following molecular formulae are alkanes?

C_2H_2 C_3H_8 C_4H_8 C_8H_{18} $C_{10}H_{20}$

4 It is possible to write a general formula for alkanes in the form of C_xH_y.

a) Suppose x equals n. If an alkane has n carbon atoms, how many hydrogen atoms will it have? (Hint: In long-chain alkanes, every carbon atom has 2 hydrogen atoms, except the end carbon atoms, each of which has 1 extra hydrogen atom.)

b) What is the value of y in terms of n?

c) Write the general formula for alkanes in terms of C, H and n.

5 **a)** Draw the skeletal formula of butane, C_4H_{10}.

b) Why is it not possible to draw a skeletal formula of methane?

6 **a)** Use a molecular model kit to construct a model of propane.

b) Connect one more carbon atom to the carbon chain in your model of propane to produce butane.

c) Connect a carbon atom to a different place on the carbon chain in your model of propane to produce an alkane which is not butane.

d) Draw the skeletal formula of this alternative structure of C_4H_{10}.

e) How many alternative structures of molecular formula C_5H_{12} can you make? Draw a skeletal formula of each one.

6.1.4 Naming simple organic compounds

The International Union of Pure and Applied Chemistry (IUPAC) is the recognised authority for naming chemical compounds. IUPAC has developed systematic names based on a set of rules. These IUPAC rules make it possible to work out the structure of a compound from its name and to work out its name from its structure. The names of organic compounds are based on the longest chain or main ring of carbon atoms in the carbon skeleton. The IUPAC names of the first ten unbranched alkanes are shown in Table 6.1.4.

Table 6.1.4 Names and molecular formulae of the first ten alkanes with unbranched chains of carbon atoms.

Number of carbon atoms	Molecular formula	Name
1	CH_4	Methane
2	C_2H_6	Ethane
3	C_3H_8	Propane
4	C_4H_{10}	Butane
5	C_5H_{12}	Pentane
6	C_6H_{14}	Hexane
7	C_7H_{16}	Heptane
8	C_8H_{18}	Octane
9	C_9H_{20}	Nonane
10	$C_{10}H_{22}$	Decane

Table 6.1.5 The structures of alkyl groups.

Alkyl group	Formula
Methyl	$CH_3–$
Ethyl	$CH_3CH_2–$
Propyl	$CH_3CH_2CH_2–$
Butyl	$CH_3CH_2CH_2CH_2–$

Tip

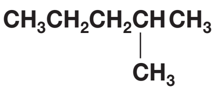
When writing names, use a comma between two numbers, but a hyphen between a number and letter.

Naming alkanes

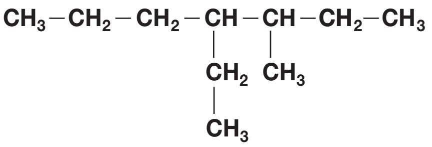
In naming an alkane, it is important to follow the IUPAC rules.

1 Look for the longest unbranched chain of carbon atoms in the carbon skeleton of the molecule and name that part of the compound. So:

$CH_3CH_2CH_2CH_2CH_3$ is pentane

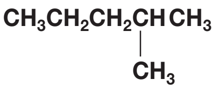


$CH_3CH_2CH_2\underset{\displaystyle\overset{|}{CH_3}}{CH}CH_3$ is pentane with a CH_3 group attached

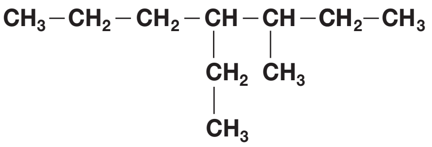


$CH_3-CH_2-CH_2-\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{CH}-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-CH_2-CH_3$ is heptane with one CH_3 and one CH_3CH_2 group attached

2 Identify the alkyl groups attached to the longest unbranched chain. The simplest alkyl group is the methyl group, CH_3, which is methane with one hydrogen atom removed. Alkyl groups are alkane molecules minus one hydrogen atom (Table 6.1.5). So:



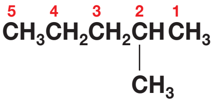
$CH_3CH_2CH_2\underset{\displaystyle\overset{|}{CH_3}}{CH}CH_3$ has a methyl side group



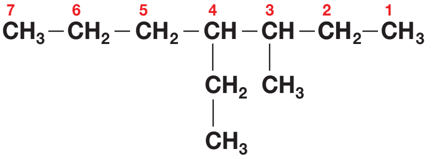
$CH_3-CH_2-CH_2-\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{CH}-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-CH_2-CH_3$ has an ethyl side group and a methyl side group

3 Number the carbon atoms in the main chain to identify which carbon atoms the side groups are attached to.

4 Name the compound using the name of the longest unbranched chain, prefixed by the names of the side groups and the numbers of the carbon atoms to which they are attached. The numbering of the carbon atoms can be from either the left or the right to give the name with the lowest numbers. So:

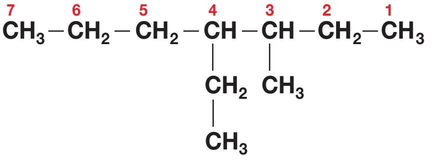


$\overset{5}{CH_3}\overset{4}{CH_2}\overset{3}{CH_2}\underset{\displaystyle\overset{|}{CH_3}}{\overset{2}{CH}}\overset{1}{CH_3}$ is 2-methylpentane – *not* 4-methylpentane



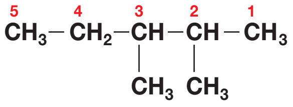
$\overset{7}{CH_3}-\overset{6}{CH_2}-\overset{5}{CH_2}-\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{\overset{4}{CH}}-\underset{\begin{array}{c}|\\CH_3\end{array}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$ is 4-ethyl-3-methylheptane – *not* 4-ethyl-5-methylheptane

5 When there is more than one type of side group, they should be arranged alphabetically. So:



$\overset{7}{CH_3}-\overset{6}{CH_2}-\overset{5}{CH_2}-\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{\overset{4}{CH}}-\underset{\begin{array}{c}|\\CH_3\end{array}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$ is 4-ethyl-3-methylheptane – *not* 3-methyl-4-ethylheptane

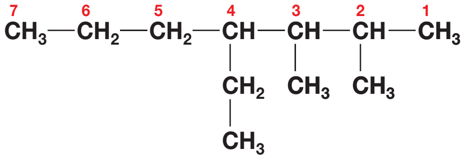
6 When there are two or more of the same side group, add the prefix 'di', 'tri', 'tetra' and so on. So:



$\overset{5}{CH_3}-\overset{4}{CH_2}-\underset{\substack{|\\CH_3}}{\overset{3}{CH}}-\underset{\substack{|\\CH_3}}{\overset{2}{CH}}-\overset{1}{CH_3}$

is 2,3-dimethylpentane –
not 3,4-dimethylpentane and
not 2-methyl-3-methylpentane

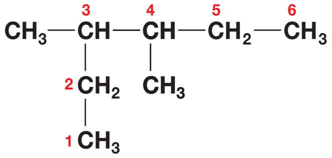
Using the prefix 'di', 'tri', 'tetra' and so on does not change the alphabetical order of the side groups, so:



$\overset{7}{CH_3}-\overset{6}{CH_2}-\overset{5}{CH_2}-\underset{\substack{|\\CH_2\\|\\CH_3}}{\overset{4}{CH}}-\underset{\substack{|\\CH_3}}{\overset{3}{CH}}-\underset{\substack{|\\CH_3}}{\overset{2}{CH}}-\overset{1}{CH_3}$

is 4-ethyl-2,3-dimethylheptane.

Beware that the longest carbon chain may involve a side group:



$CH_3-\underset{\substack{|\\{}^{2}CH_2\\|\\{}^{1}CH_3}}{\overset{3}{CH}}-\underset{\substack{|\\CH_3}}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_3}$

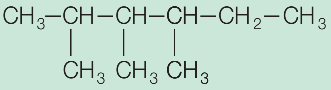
is 3,4-dimethylhexane (numbering from either end of the six-carbon chain) – *not* 2-ethyl-3-methylpentane

Test yourself

11 Name the following alkanes.

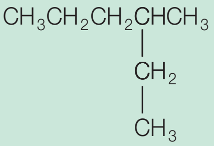
a) $CH_3(CH_2)_6CH_3$

b)



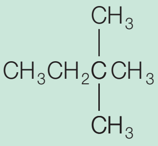
$CH_3-\underset{\substack{|\\CH_3}}{CH}-\underset{\substack{|\\CH_3}}{CH}-\underset{\substack{|\\CH_3}}{CH}-CH_2-CH_3$

c)



$CH_3CH_2CH_2\underset{\substack{|\\CH_2\\|\\CH_3}}{C}HCH_3$

d)



$CH_3CH_2\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}CH_3$

12 Draw the displayed formulae of the following alkanes:

a) 2-methylpropane **b)** 2,3-dimethylbutane.

13 Draw the structural formulae and the skeletal formulae of the following alkanes:

a) 3,3,4-trimethylheptane **b)** 2-methylbutane

c) 3-ethyl-2-methyl-5,5-dipropyldecane.

Tip

Make sure you understand that names which include 1-methyl or 2-ethyl must be wrong (unless the compound contains a ring).

Naming alkenes

Ethene ($CH_2=CH_2$) and propene ($CH_3CH=CH_2$) are the first two members of the homologous series of alkenes with the functional group $>C=C<$.

Alkenes are named using the same general rules as alkanes, with the suffix -ene instead of -ane, sometimes prefixed by a number to indicate the position of the double bond in the chain.

With ethene and propene there is no need to number the carbon atoms because the double bond must be between carbon atoms 1 and 2. But with a chain of four or more carbon atoms, the double bond may be in more than one position.

Tip

When more than one double bond is present, the letter ‘a’ is included between the consonants ‘t’ and ‘d’, as in butadiene, or more fully buta-1,3-diene, $H_2C{=}CH{-}CH{=}CH_2$.

Thus, the molecule $CH_2{=}CHCH_2CH_3$ is named but-1-ene. Although the double bond links carbon atoms 1 and 2, the lower number 1 is used to indicate the start of the bond.

Using the same rule, $CH_3CH{=}CHCH_3$ is named but-2-ene.

The methods of naming organic compounds with other functional groups will be explained as they arise.

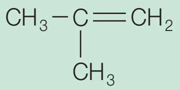
Tip

Ethene was shown in Table 6.1.1 as $H_2C{=}CH_2$, but is shown at the start of this section as $CH_2{=}CH_2$. Both representations are accepted as correct structural formulae, although $H_2C{=}CH_2$ is preferred by some because it shows the double bond between carbon atoms more clearly.

Test yourself

14 Name the following alkenes:

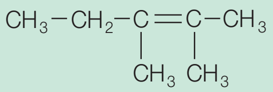
a)



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$$

b) $CH_3CH_2CH_2CH{=}CHCH_3$

c)



$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$$

15 Draw the structural formulae of the following alkenes:

a) 2-methylbut-2-ene

b) 3,4-dimethylpent-1-ene.

16 Draw the skeletal formulae of the following alkenes:

a) 2-methylbut-2-ene

b) 3,4-dimethylpent-1-ene.

6.1.5 Isomerism

Key term

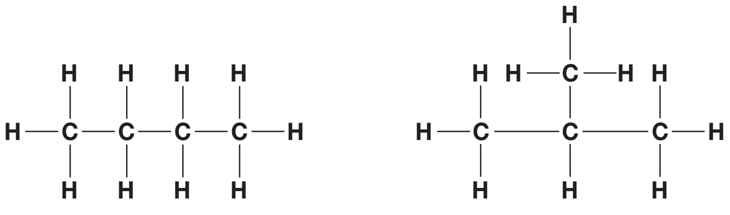
Structural isomers are compounds with the same molecular formula but different structural formulae.

Another reason why carbon forms so many compounds is that it is sometimes possible to join the same atoms together in different ways. Consider, for example, the molecular formula C_4H_{10}. You probably realise already that this could be butane – but there is another compound, 2-methylpropane, which also has the molecular formula C_4H_{10}. Both are shown in Figure 6.1.10. Compounds like butane and 2-methylpropane, which have the same molecular formula but different structural formulae, are called **structural isomers**.

There are two structural isomers of C_4H_{10}, three structural isomers of C_5H_{12} and five structural isomers of C_6H_{14}. Table 6.1.6 shows that the number of structural isomers of the alkanes increases very quickly.

It is useful to divide structural isomers into three different types – chain isomers, position isomers and functional group isomers.

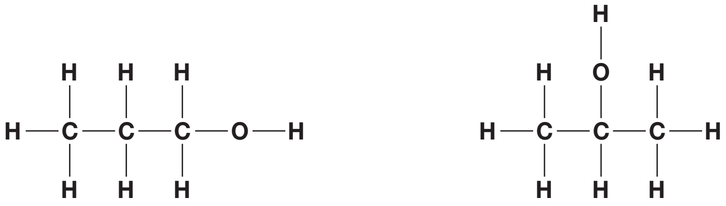
- *Chain isomers* have different chains of carbon atoms (Figure 6.1.10).
- *Position isomers* have different positions of the same functional group (Figure 6.1.11).
- *Functional group isomers* have different functional groups (Figure 6.1.12).



butane

2-methylpropane

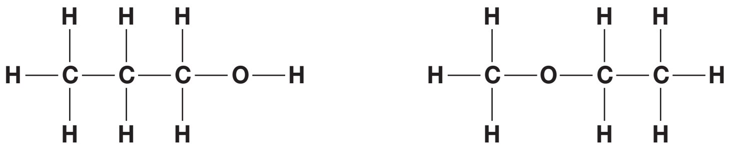
Figure 6.1.10 Structural isomers of C_4H_{10}.



propan-1-ol

propan-2-ol

Figure 6.1.11 Propan-1-ol and propan-2-ol are both alcohols like ethanol, CH_3CH_2OH. All alcohols contain the –OH group. In propan-1-ol and propan-2-ol the –OH group is in a different position on the carbon chain.



propan-1-ol
(an alcohol)

methoxyethane
(an ether)

Figure 6.1.12 Propan-1-ol is an alcohol with the –OH functional group. Methoxyethane is an ether with the C–O–C functional group. Both these compounds have the same molecular formula, C_3H_8O.

Notice that the word describing the type of structural isomer (chain, position and functional group) tells you how the isomers differ from each other.

Test yourself

17 a) Draw displayed formulae of the three structural isomers with the molecular formula C_5H_{12} and name them.

b) What type of structural isomerism is shown by the three isomers in part (a)?

Table 6.1.6 The number of structural isomers of the alkanes.

Number of carbons	Number of isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
11	159
12	355
13	802
14	1 858
15	4 347
20	366 319
25	36 797 588
30	4 111 846 763
40	62 491 178 805 831 or 62 481 801 147 341 opinions differ!

18 a) Draw skeletal formulae of the five structural isomers with the molecular formula C_6H_{14}.

b) Identify the position isomers in your answer to part (a).

19 a) Draw structural formulae of the alkene structural isomers with molecular formula C_4H_8 and name them.

b) Draw skeletal formulae of the two functional group isomers of C_4H_8 which are not alkenes.

Key terms

Addition is a reaction in which two molecules add together to form a single product.

Substitution is a reaction in which one atom or group is replaced by another atom or group.

Elimination is a reaction which produces an unsaturated product by loss of atoms or groups from adjacent carbon atoms.

Hydrolysis is a reaction in which a compound splits apart in a reaction involving water.

6.1.6 Types of organic reaction

Almost all organic molecules will burn, so most organic molecules can be oxidised in redox reactions. Apart from redox, the type of reaction depends on the structure of the molecule.

If a molecule contains a double bond, it is said to be unsaturated and another molecule can join on to it in an **addition** reaction.

If a molecule is saturated, that is it contains only single bonds, then it can react in two possible ways:

- An atom or group can be replaced in a **substitution** reaction.
- Adjacent atoms or groups can be removed to form an unsaturated molecule in an **elimination** reaction.

Both saturated and unsaturated molecules undergo **hydrolysis** reactions which may involve substitution or addition steps.

Addition – adding bits to molecules

Addition reactions are characteristic of unsaturated compounds with double bonds. During an addition reaction, two molecules add together to form a single product. Ethene, for example, reacts with bromine to form the colourless addition product 1,2-dibromoethane (Section 6.2.9).

All types of unsaturated molecules can be saturated by reaction with hydrogen in the presence of a catalyst in a hydrogenation reaction. Addition of hydrogen can also be described as reduction.

Hydrogen adds to C=C double bonds in alkenes such as propene in the presence of a platinum or palladium catalyst at room temperature, or on heating to 150 °C in the presence of a nickel catalyst (Figure 6.1.13).

Addition to alkenes is considered in more detail in Section 6.2.9.

Tip

The atom economy of an addition reaction is always 100% because only one product is formed.

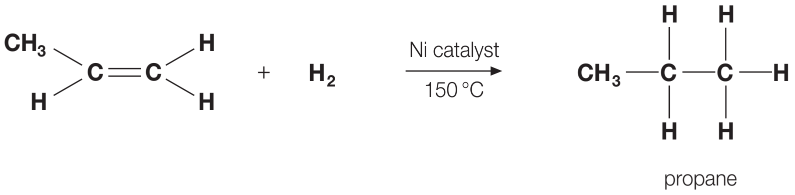


Figure 6.1.13 The hydrogenation of propene.

Polymerisation – making long chains

Under the right conditions, small molecules with double bonds can add to each other and join up in long chains to form polymers. This is called **addition polymerisation** (Section 6.2.12).

For instance, ethene molecules can join together to form poly(ethene), a substance commonly known as polythene (Figure 6.1.14).

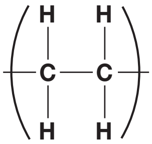


Figure 6.1.14 The repeating unit of poly(ethene).

Key term

Addition polymerisation is an addition reaction in which small molecules, called monomers, join together forming a giant molecule, called a polymer.

Elimination – splitting bits off from molecules

An elimination reaction splits off a simple molecule, such as water or hydrogen chloride, from a larger molecule leaving a double bond.

Examples of elimination reactions are:

- the removal of a hydrogen halide from a halogenoalkane in alkaline conditions to produce an alkene (Section 6.3.4)

  $CH_3CH_2CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH{=}CH_2 + H_2O + Br^-$

  1-bromobutane → but-1-ene

- the removal of water from an alcohol in acidic conditions to produce an alkene (Section 6.3.8).

  $CH_3CH_2CH_2OH \xrightarrow{\text{conc. } H_2SO_4} CH_3CH{=}CH_2 + H_2O$

  propan-1-ol → propene

Tip

Addition reactions convert unsaturated compounds into saturated.
Elimination reactions convert saturated compounds into unsaturated.

Substitution – replacing one or more atoms by others

Substitution reactions replace an atom or a group of atoms by another atom or group of atoms. An example is the reaction of butan-1-ol with hydrogen bromide to make 1-bromobutane (Section 6.3.4 Activity).

$CH_3CH_2CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2CH_2Br + H_2O$

butan-1-ol → 1-bromobutane

Substitution reactions are characteristic of halogenoalkanes (Section 6.3.4).

Other examples of substitution reactions include the replacement of hydrogen atoms in alkanes by chlorine or bromine atoms in the presence of ultraviolet light (Section 6.2.3).

$CH_4 + Cl_2 \xrightarrow{\text{UV light}} CH_3Cl + HCl$

methane → chloromethane

Hydrolysis – splitting apart with water

The word ‘hydrolysis’ comes from two other words – ‘hydro’ related to water and ‘lysis’ meaning splitting. So, the term hydrolysis is used to describe any reaction in which water causes another compound to split apart. Hydrolysis reactions are often catalysed by acids or alkalis. They are often substitution reactions in which the chemical attack is by nucleophiles such as water molecules or hydroxide ions.

An example of hydrolysis is the reaction of halogenoalkanes with water. In this case, bonds in both the water and halogenoalkanes split to form alcohols and hydrogen halides (Section 6.3.4). The reaction is very slow in the absence of alkali.

$$\underset{\text{2-bromopropane}}{CH_3CHBrCH_3} + H_2O \rightarrow \underset{\text{propan-2-ol}}{CH_3CHOHCH_3} + HBr$$

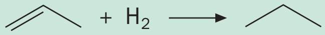
Test yourself

20 Classify the following reactions as redox, addition, substitution, elimination or hydrolysis.

a) $C_2H_5OH \rightarrow C_2H_4 + H_2O$

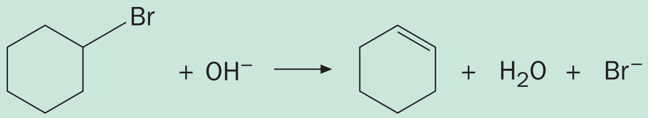
b) $CH_3COOCH_2CH_3 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

c)



d) $CH_3CHBrCH_2CH_3 + OH^- \rightarrow CH_3CH(OH)CH_2CH_3 + Br^-$

e)



21 Give the structures and names of the products of the addition reactions of but-2-ene with:

a) hydrogen

b) chlorine

c) hydrogen bromide.

22 Write equations for the elimination reactions which occur when:

a) 2-bromopropane reacts with a hot solution of potassium hydroxide in ethanol

b) butan-1-ol is dehydrated by passing over a hot catalyst.

23 Draw a structure to represent the addition polymer PTFE, poly(tetrafluoroethene), formed from tetrafluoroethene.

24 Write equations for:

a) the substitution reaction in which ethane reacts with bromine to form bromoethane and one other product

b) the substitution reaction in which 1-bromopropane reacts with sodium hydroxide to form propan-1-ol and one other product

c) the hydrolysis reaction in which the ester ethyl ethanoate, $CH_3COOCH_2CH_3$, reacts with water to form ethanoic acid and one other product.

6.1.7 Introduction to the mechanisms of organic reactions

Reactions between ionic compounds in solution are almost instantaneous, the ions simply collide (see Section 9.4). However, when organic compounds react the covalent bonds in the molecules require energy to break, and a sequence of bond breaking and bond forming steps can occur as reactants turn into products. This sequence is called a *mechanism* and chemists have used great ingenuity to work out mechanisms. They began with simple reactions but are now using their knowledge to explain what happens during industrial processes and in living cells, where enzymes control biochemical processes.

There are two ways in which a bond can break – homolytically or heterolytically.

Homolytic bond breaking

A covalent bond involves a shared pair of electrons. If the bond breaks homolytically then each atom keeps one electron – this is 'equal splitting' (homolytic fission) (Figure 6.1.15).

Tip

The use of curly half-arrows is not expected in this mechanism.

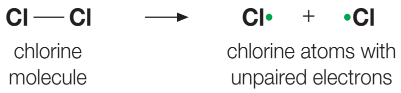


Figure 6.1.15 Homolytic bond breaking. The covalent bond breaks and the atoms separate, each taking one of the shared pair of electrons.

This type of splitting produces fragments with unpaired electrons. A fragment of this type is called a **free radical**. Free radicals (often simply called radicals) exist for a short time during a reaction, but quickly react to form new products. So, free radicals are intermediates which form during a reaction but then disappear as the reaction is completed.

Key term

A **free radical** is a species with an unpaired electron.

Chemists use a single dot to represent the unpaired electron on a radical. Other paired electrons in the outer shells are not usually shown.

Free radicals often occur in reactions taking place in the gas phase or in a non-polar solvent. Ultraviolet light can speed up free-radical reactions.

Examples of free-radical processes include the thermal cracking of hydrocarbons (Section 6.2.4), the burning of petrol and other alkanes (Section 6.2.3) and the substitution reactions of alkanes with halogens (Section 6.2.3). Free-radical reactions are important high in the atmosphere where gases are exposed to intense ultraviolet radiation from the Sun. The reactions which form and destroy the ozone layer are free-radical reactions.

Heterolytic bond breaking

When a covalent bond breaks heterolytically, one atom takes both of the electrons from the bond, the other atom takes none (Figure 6.1.16).

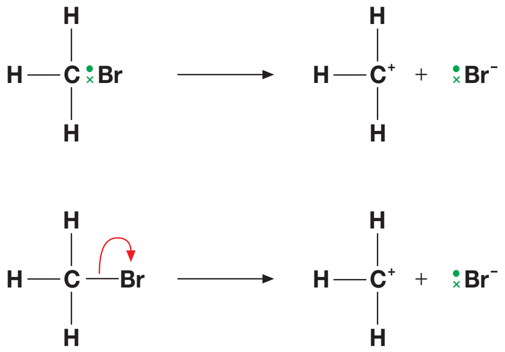


Figure 6.1.16 Heterolytic bond breaking. Note the use of a curly arrow to show what happens to the electrons as the bond breaks. A curly arrow shows the movement of a pair of electrons. The covalent bond breaks and the atoms separate, with one atom taking both electrons in the shared pair. The arrow starts from the pair of electrons that is moving. The head of the arrow points to where the electron pair will be after the change.

Tip

The prefix 'homo' means 'the same' or 'similar'. Chemical terms which include this prefix include homolytic fission, homogeneous catalyst and homologous series.

The prefix 'hetero' means 'different'. Chemical terms which include this prefix include heterolytic fission and heterogeneous catalyst.

Heterolytic bond breaking (heterolytic fission) produces ionic intermediates, such as CH_3^+ and Br^- in reactions like that shown in Figure 6.1.16. This type of bond breaking is favoured when reactions take place in polar solvents such as water. Often, the bond which breaks is already polar (Section 2.5) with a δ+ end and a δ− end, like the C–Br bond in Figure 6.1.17.

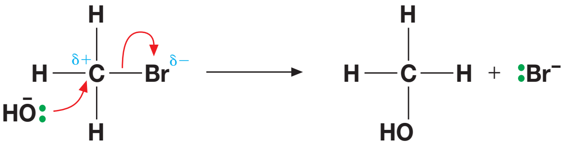


Figure 6.1.17 A nucleophile attacking a δ+ carbon leading to heterolytic bond breaking.

Some of the reagents which initiate reactions seek out the δ+ end of polar bonds. These are called **nucleophiles** and will always have a lone pair of electrons to donate.

Other reagents seek out the δ− end of polar bonds or the electron dense regions in molecules. These are called **electrophiles**.

Key terms

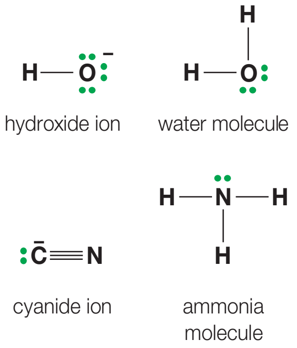
Nucleophiles are electron pair donors. They are negative ions or molecules with a lone pair of electrons that attack positive ions or positive centres in molecules.

Electrophiles are electron pair acceptors. They are positive ions or molecules with a vacant orbital that attack negative ions or negative centres in molecules.

Nucleophiles

Nucleophiles are molecules or ions with a lone pair of electrons which can form a new covalent bond (Figure 6.1.18). They are electron-pair donors. Nucleophiles are reagents which attack molecules that have a partial positive charge, δ+, so they seek out positive charges – they are 'nucleus loving'.

The substitution reactions of halogenoalkanes involve nucleophiles (Section 6.3.4).



hydroxide ion

water molecule

cyanide ion

ammonia molecule

Figure 6.1.18 Examples of nucleophiles.

Electrophiles

Electrophiles are molecules or ions that attack negative ions or parts of molecules which are rich in electrons with negative centres, δ−. They are 'electron-loving' reagents. Electrophiles form a new bond by accepting a pair of electrons from the molecule or ion attacked during a reaction.

An example of an electrophile is the H atom at the δ+ end of the H–Br bond in hydrogen bromide. See, for example, the electrophilic addition reactions of alkenes (Section 6.2.10).

Test yourself

25 Write equations (without curly arrows) to show how:

- **a)** a bromine molecule breaks homolytically
- **b)** a hydrogen bromide molecule breaks heterolytically
- **c)** a C–H bond in a methane molecule breaks homolytically.

26 Write equations including curly arrows to show how:

- **a)** a bromide ion reacts with CH_3^+ to form bromomethane
- **b)** a hydroxide ion reacts with a hydrogen ion to form water
- **c)** an ammonia molecule reacts with water to form an ammonium ion and a hydroxide ion.

27 In each of the following examples decide whether the reagent attacking the carbon compound is a free radical, a nucleophile or an electrophile:

- **a)** $CH_3CH_2I + H_2O \rightarrow CH_3CH_2OH + HI$
- **b)** $CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2Br$
- **c)** $CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$
- **d)** $CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$

6.1.8 Investigating reaction mechanisms

The techniques which chemists use to study reactions are becoming more and more sophisticated. With the help of laser beams and spectroscopy, it is now possible to follow extremely fast reactions and to watch molecules breaking apart and rearranging themselves in fractions of a second. This section outlines other ways in which reaction mechanisms can be studied.

Labelling with isotopes

Chemists can use isotopes as markers to track what happens to particular atoms during a chemical change. They replace atoms of the normal isotope of an element in a molecule with a different isotope (Section 1.4).

Isotopes of an element have identical chemical properties, so it is possible to use them to follow what happens during a change without altering the normal course of a reaction. Radioactive isotopes can usually be tracked fairly easily and conveniently by detecting their radiation. The fate of non-radioactive isotopes can be followed by analysing samples with a mass spectrometer (Section 7.1).

Trapping intermediates

An important key to understanding reaction mechanisms was the realisation that most reactions do not take place in one step, as implied by the balanced equation. Instead, most reactions involve a series of steps. In the course of these mechanisms, atoms, molecules and ions, which do not appear in the balanced equation, exist as intermediates as chemicals change from the reactants to the products.

Activity

Investigating the mechanism of a hydrolysis reaction

Alcohols react with carboxylic acids to form esters. Hydrolysis splits esters back to the alcohol and acid. Isotopic labelling has been used to investigate the mechanism of this hydrolysis reaction (Figure 6.1.19). The researchers used water labelled with oxygen-18 instead of the normal oxygen-16 isotope. After hydrolysis with $H_2{}^{18}O$, they found that the heavier oxygen atoms from the water ended up in the acid and not in the alcohol. In this way they were able to identify exactly which bond breaks during hydrolysis of the ester.

1. Why is the reaction of an ester with water described as ‘hydrolysis’?
2. How do atoms of the oxygen-18 and oxygen-16 isotopes differ?
3. Why do oxygen-18 and oxygen-16 isotopes have the same chemical properties?
4. What method of analysis can be used to distinguish ethanoic acid molecules with ^{18}O atoms from those with ^{16}O atoms? (Neither isotope of oxygen is radioactive.)
5. Look closely at Figure 6.1.19. Which bond in the ester breaks during the reaction?
6. Where would the oxygen-18 atoms have appeared if the mechanism involved breaking the other C—O bond in the ester?

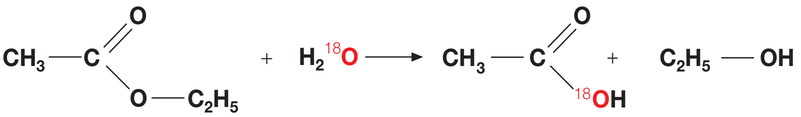


Figure 6.1.19 Use of labelling to investigate bond breaking during the hydrolysis of an ester.

Chemists can often use spectroscopy (Chapter 7) to detect intermediates which exist for only a short time during a reaction. Intermediates can also be detected chemically. This can be done by adding chemicals to trap the intermediates by reacting with them. This gives rise to products that would never be formed without first producing the intermediate. In this way, chemists showed that the addition of bromine to alkenes must be a two-step reaction (Section 6.2.10).

Studying reaction rates

Chemists have learned a great deal about reaction mechanisms by studying the rates of chemical reactions. This is illustrated by the mechanisms of substitution reactions of halogenoalkanes (Section 6.3.4). What these mechanisms show is that the effects of changing the concentrations of the reactants are not the same for primary and for tertiary halogenoalkanes. Taken with other evidence, this suggests that the two types of halogenoalkane react by different mechanisms.

Studying the shapes of molecules

Studying the shapes of molecules can also give clues to the details of reaction mechanisms. Part of the evidence that helped to confirm the two-step mechanism for electrophilic addition to alkenes (Section 6.2.10) came from studies of the isomers which form when bromine adds to compounds such as cyclohexene.

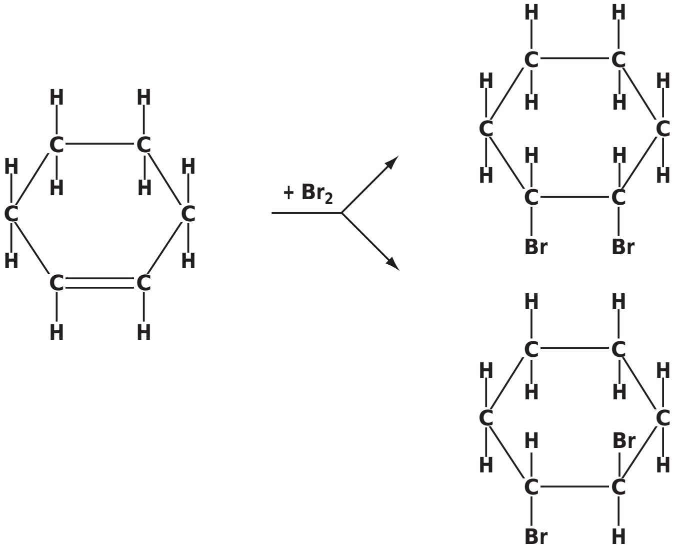


Figure 6.1.20 Two possible products when bromine adds to cyclohexene forming 1,2-dibromocyclohexane.

There are two possible isomers when bromine adds to cyclohexene. One has both bromine atoms on the same side of the ring of carbon atoms and the other has the bromine atoms on opposite sides. It turns out that the main product of the reaction is the isomer with the bromine atoms on opposite sides of the ring (trans), which is the lower structure in Figure 6.1.20. This suggests that the bromine does not add directly to alkene molecules as Br_2 molecules, but a two-stage mechanism via a positively charged carbocation occurs.

Exam practice questions

1 a) Carbon is able to form a vast number of chemical compounds. Give two reasons for this. *(2)*

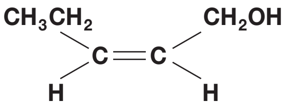
b) Petrol is a mixture of hydrocarbons containing between 6 and 10 carbon atoms. Some of these hydrocarbons are structural isomers.

  i) Explain the term 'structural isomers'. *(2)*

  ii) Some of the hydrocarbons in petrol are alkanes. Write the general formula of the alkanes and the molecular formula of an alkane that could be present in petrol. *(2)*

c) Petrol also contains cycloalkanes. Draw the structure of cyclohexane and write the general formula of cycloalkanes. *(2)*

2 The compound X below, containing two functional groups, can be extracted from oil of violets.



X

a) State the empirical and molecular formula of X and draw its skeletal formula. Explain the term 'functional group' and name the functional groups present in X. *(7)*

b) X reacts with hydrogen and a nickel catalyst in the gas phase to produce compound Y with the formula $CH_3(CH_2)_3CH_2OH$.

  i) What is the IUPAC name of Y? *(1)*

  ii) Write an equation, including state symbols, for the reaction of X with hydrogen to form Y. *(2)*

  iii) Y has two structural isomers which are also position isomers. Name these two position isomers of Y. *(2)*

  iv) Y also has structural isomers with different functional groups. Write the structural formula of one of these isomers. *(1)*

3 a) Crude oil is a mixture of many hydrocarbons. Using fractional distillation it can be separated into fractions that can be refined to produce hydrocarbons such as dodecane.

  i) What is meant by the term 'hydrocarbon'? *(1)*

  ii) One molecule of dodecane contains 12 carbon atoms. What is the molecular formula of dodecane? *(1)*

  iii) What is the empirical formula of dodecane? *(1)*

b) Decane, $C_{10}H_{22}$, is a straight-chain alkane. It reacts with chlorine in a free-radical reaction to form the compound $C_{10}H_{21}Cl$.

  i) Explain the term 'free radical'. *(2)*

  ii) Write an equation for the formation of chlorine free radicals from Cl_2. *(1)*

  iii) What type of bond fission is involved in the formation of chlorine free radicals? *(1)*

  iv) How many different structural isomers can be produced when decane reacts with chlorine to form $C_{10}H_{21}Cl$? *(1)*

  v) Draw the structural formula of one of these structural isomers. What is its name? *(2)*

4 Classify the following conversions as *addition*, *elimination*, *substitution*, *oxidation*, *reduction*, *hydrolysis* or *polymerisation* reactions. (Note that a reaction may belong to more than one category.)

a) 2-iodobutane to but-2-ene *(1)*
b) butane to 1-bromobutane *(1)*
c) but-1-ene to 1,2-dichlorobutane *(1)*
d) butanal to butanoic acid *(1)*
e) 1-bromobutane to butan-1-ol *(1)*
f) buta-1,3-diene to synthetic rubber. *(1)*

5 a) i) Explain the term 'electrophile', giving an example. *(2)*

  ii) Use symbols to describe the mechanism of the electrophilic addition of hydrogen bromide to ethene. Show any relevant dipoles. *(5)*

b) i) Explain the term 'nucleophile', giving an example. *(2)*

  ii) Use symbols to describe the mechanism of nucleophilic substitution during the reaction of hydroxide ions with bromoethane. Show any relevant dipoles. *(5)*

● **6** **a)** Discuss the circumstances that favour homolytic bond breaking and those that favour heterolytic bond breaking during organic reactions. *(6)*

b) Explain why it is helpful for chemists to classify reagents as free radicals, electrophiles or nucleophiles. *(4)*

● **7** Complete combustion of 0.292 g of a compound containing carbon, hydrogen and oxygen formed 408 cm^3 of carbon dioxide and 0.308 g of water. (Molar volume of a gas is 24.0 $\text{dm}^3\,\text{mol}^{-1}$.)

a) Calculate the empirical formula of the compound. *(6)*

b) The molecular formula of the compound is the same as its empirical formula. Explain why the molecule must either be cyclic or contain a double bond. Draw the structural formula of one cyclic compound and the structural formulae of three unsaturated compounds that are functional group isomers with this molecular formula. *(5)*

● **8** The reaction of ethanol with 50% sulfuric acid and potassium bromide produces 1-bromobutane as the main product. Side reactions also form ethene and some ethoxyethane, $C_2H_5{-}O{-}C_2H_5$. The first step in all the reactions is for ethanol to gain a hydrogen ion, H^+, from the acid.

a) Draw a diagram, with a curly arrow, to show ethanol forming a bond with H^+. *(2)*

b) The main product forms by reaction of the intermediate from part (a) with bromide ions. Draw a diagram with curly arrows to show that this is a nucleophilic substitution reaction. *(2)*

c) Draw a diagram with curly arrows to show how an elimination reaction turns the intermediate from part (a) into an alkene. *(2)*

d) Identify the nucleophile that reacts with the intermediate from part (a) to form ethoxyethane and explain how it acts as a nucleophile. *(2)*

e) Ethoxyethane is unaffected by acidified potassium dichromate(VI).

- **i)** Draw a functional group isomer of ethoxyethane that is also unaffected by acidified potassium dichromate(VI). *(1)*
- **ii)** Describe how the isomer from part (e)(i) and ethoxyethane could be distinguished by a physical test and by a chemical test. *(4)*

6.2 Hydrocarbons: alkanes and alkenes

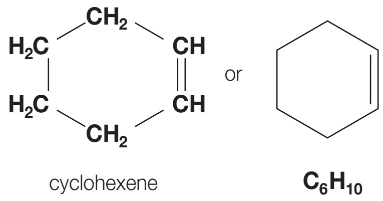


Figure 6.2.1 Structures of the aliphatic hydrocarbon cyclohexene, which is a cycloalkene.

Key terms

Hydrocarbons are compounds of carbon and hydrogen only.

Aliphatic hydrocarbons have branched or unbranched chains of carbon atoms or rings of carbon atoms.

Aromatic hydrocarbons or **arenes** contain rings of carbon atoms in which there are delocalised electrons.

Saturated compounds have only single bonds between atoms in their molecules.

6.2.1 Types of hydrocarbon

Hydrocarbons make up the majority of crude oil – the source of most fuels and the main raw material for the chemical industry. Hydrocarbons are compounds containing hydrogen and carbon only. The most common and most important hydrocarbons are alkanes and alkenes.

There are two types of hydrocarbon.

- **Aliphatic hydrocarbons** are those with chains of carbon atoms which may be branched or unbranched and with rings that are not aromatic. Alkanes and alkenes such as cyclohexene (Figure 6.2.1) are examples of aliphatic compounds.
- **Aromatic hydrocarbons**, such as benzene, methylbenzene and naphthalene, are ring compounds in which there are delocalised electrons (Figure 6.2.2). They are called aromatic because of their smells (aromas). These hydrocarbons are sometimes called **arenes**.

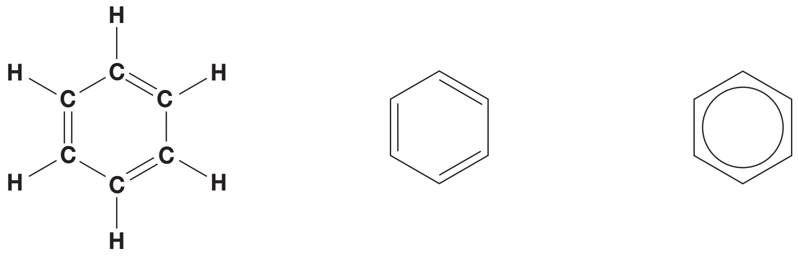


Figure 6.2.2 Representations of the structure of benzene. At one time, chemists thought that the ring structure in benzene had three double and three single bonds. X-ray studies have shown that all six bonds in the ring are identical and that each carbon atom contributes one electron to a cloud of delocalised electrons. This has led to the third structure with a ring inside a hexagon.

6.2.2 Alkanes

Alkanes are the hydrocarbons which make up most of crude oil and natural gas. Alkanes form a series of organic compounds with the general formula C_nH_{2n+2}.

Alkanes are **saturated compounds** – they have only single bonds between the atoms in their molecules. The term 'saturated' is also used for compounds with saturated hydrocarbon chains, such as saturated fats and fatty acids in food (Figure 6.2.3). If eaten in excess, saturated fats lead to high levels of cholesterol in the blood which causes furring and blocking of the arteries. Unfortunately, not all unsaturated fats are good for health – *trans* fats should also be avoided (see Section 6.2.9).

Figure 6.2.3 The saturated fats in foods such as beef burgers and doughnuts contain alkyl groups with long chains of carbon atoms.

Physical properties

Alkanes are composed of simple molecules which are held together by only weak intermolecular forces (Section 2.6). As the molecules get larger, the intermolecular forces increase, and therefore the melting and boiling temperatures rise as the number of carbon atoms per molecule increases.

At room temperature and pressure, alkanes in the range C_1 to C_4 are gases, those in the range C_5 to C_{17} are liquids, while those from C_{18} upwards are solids.

Tip

All combustion reactions are exothermic (Section 8.2). So an alkane plus oxygen is unstable with respect to the products of oxidation which are at a lower energy. But fuels do not spontaneously ignite without the input of sufficient activation energy (Section 9.4). The combustion reaction does not take place and the rate of the reaction is effectively zero without, for example, a spark to provide this activation energy. So although energetics might predict that a reaction should occur, kinetics prevents it happening at room temperature. This kinetic stability is extremely fortunate because, without it, no fuels could be stored for future use.

Test yourself

1 a) Write the molecular formulae and names of the first four members of the alkanes.

b) What is the difference in molecular formula from one alkane to the next?

2 Explain why the general formula of the alkanes is C_nH_{2n+2}.

3 Write the molecular formulae of the first liquid alkane and of the first solid alkane at room temperature.

6.2.3 Chemical reactions of the alkanes

The bond enthalpies of C–C and C–H bonds are relatively high, so the bonds in alkanes are difficult to break. In addition, these bonds are non-polar (Section 2.5). This means that alkanes are very unreactive with ionic reagents in water – such as acids, alkalis, oxidising agents and reducing agents. There are, however, three important reactions of alkanes involving homolytic bond breaking and free radicals (Section 6.1.7). These three important reactions are combustion (burning), halogenation and cracking (Section 6.1.7).

Reaction with oxygen – combustion

Many common fuels consist mainly of alkanes. Natural gas is mainly methane, Calor Gas® (Figure 6.2.4) is mainly propane and Gaz® is mainly butane. In a plentiful supply of air or oxygen, the alkanes are completely oxidised to carbon dioxide and water. The reaction is highly exothermic.

$$\underset{\text{butane}}{C_4H_{10}(g)} + 6\tfrac{1}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) \quad \Delta_c H^{\ominus}\ -2876\,\text{kJ mol}^{-1}$$

Figure 6.2.4 Red Calor Gas® cylinders contain propane for use as a fuel.

If the air is in short supply, the products include soot (carbon) and highly toxic carbon monoxide as well as carbon dioxide (see Section 6.2.5). Alkanes are kinetically stable in the air (oxygen), but they are energetically (thermodynamically) unstable with respect to the products of oxidation.

The combustion of alkanes involves a free-radical mechanism, which occurs rapidly in the gas phase. This means that liquid and solid alkanes must vaporise before they burn and it explains why less volatile alkanes burn less easily.

The burning of alkanes is immensely important in any advanced, technological society. It is used to generate energy of one kind or another in power stations, furnaces, domestic heaters, cookers, candles and vehicles. Unfortunately this mass burning of alkanes is now accepted to be a major cause of global warming and the increased greenhouse effect (Section 6.2.5).

Reactions with chlorine and bromine (halogenation)

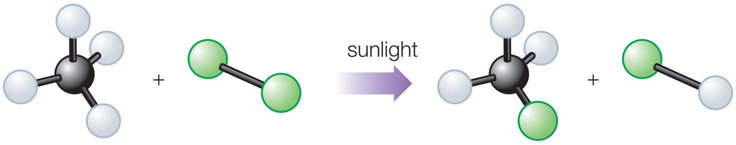
Alkanes react with chlorine and bromine, either on heating or on exposure to ultraviolet light. During the reactions, hydrogen atoms in the alkane molecules are replaced (substituted) by halogen atoms. These are described as **substitution reactions**.

Key term

A **substitution reaction** is one in which an atom, or group of atoms, is replaced by another atom, or group of atoms.

Any of the hydrogen atoms in an alkane may be replaced, and the reaction can continue until all the hydrogen atoms have been substituted by halogen atoms. Consequently, the product is a mixture of compounds.

In strong sunlight, methane and chlorine react explosively. The initial products are chloromethane, CH_3Cl, and hydrogen chloride (Figure 6.2.5).



$$CH_4(g) + Cl_2(g) \xrightarrow{\text{sunlight}} CH_3Cl(g) + HCl(g)$$

Figure 6.2.5 The equation and models representing the initial substitution reaction of methane with chlorine.

The reaction involves breaking some bonds – for which energy must be supplied – and making new bonds – when energy is released. Possible reaction mechanisms can be tested using bond enthalpies (energies) and this leads to a probable reaction mechanism.

The reaction between methane and chlorine does not occur in the dark because the molecules do not have enough energy for bonds to break when they collide. But in ultraviolet light, the energy provided by absorbed photons is 400 kJ mol^{-1}. This is enough to cause homolytic fission of chlorine molecules into free radicals:

$$Cl_2 \rightarrow Cl\bullet + Cl\bullet \qquad \Delta H = +242\,\text{kJ mol}^{-1}$$

But this is not enough for the homolytic fission of methane, which requires 435 kJ mol^{-1}:

$$CH_4 \rightarrow CH_3\bullet + H\bullet \qquad \Delta H = +435\,\text{kJ mol}^{-1}$$

and definitely not enough for the heterolytic fission of either chlorine or methane:

$$Cl_2 \rightarrow Cl^+ + Cl^- \qquad \Delta H = +1130\,\text{kJ mol}^{-1}$$

$$CH_4 \rightarrow H^+ + CH_3^- \qquad \Delta H = +1700\,\text{kJ mol}^{-1}$$

These figures suggest that ultraviolet light starts the reaction by splitting chlorine molecules into chlorine atoms (free radicals). This stage is called **initiation**.

Key terms

Free-radical substitution is the replacement of hydrogen atoms in a molecule by halogen atoms in a reaction which involves free radicals.

Free-radical chain reactions involve three stages:

initiation – the step which produces free radicals from molecules

propagation – steps which form products and more free radicals

termination – steps which remove free radicals by turning them into molecules.

A **chain** reaction occurs when a product in a reaction can react with a starting material so the reaction continues.

The chlorine atoms, each with an unpaired electron, are highly reactive. They remove hydrogen atoms from methane molecules to form hydrogen chloride and a new free radical, $CH_3\bullet$

$$Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet \qquad \Delta H = +4\,\text{kJ mol}^{-1}$$

The $CH_3\bullet$ free radical now reacts with a chlorine molecule to form chloromethane, CH_3Cl, and generate another chlorine free radical:

$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet \qquad \Delta H = -97\text{k kJ mol}^{-1}$$

The new $Cl\bullet$ free radical can react with another CH_4 molecule and the last two reactions can be repeated again and again until either all the Cl_2 or all the CH_4 is used up. These two repeated reactions create a **chain** reaction and are described as **propagation** stages.

Propagation ends when two free radicals combine. This is the **termination** stage of the reaction, which is very exothermic. There are several possible termination steps:

$$Cl\bullet + Cl\bullet \rightarrow Cl_2 \qquad \Delta H = -242\,\text{kJ mol}^{-1}$$

$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl \qquad \Delta H = -339\,\text{kJ mol}^{-1}$$

$$CH_3\bullet + CH_3\bullet \rightarrow CH_3CH_3 \qquad \Delta H = -346\,\text{kJ mol}^{-1}$$

The three stages in the **free-radical substitution** of methane with chlorine (initiation, propagation and termination) are summarised in Figure 6.2.6.

Stage 1	Initiation	$Cl\!:\!Cl \xrightarrow{\text{light}} Cl\bullet + Cl\bullet$
Stage 2	Propagation	$Cl\bullet + CH_4 \longrightarrow HCl + CH_3\bullet$ $CH_3\bullet + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$
Stage 3	Termination	$Cl\bullet + Cl\bullet \longrightarrow Cl_2$ $CH_3\bullet + Cl\bullet \longrightarrow CH_3Cl$ $CH_3\bullet + CH_3\bullet \longrightarrow CH_3CH_3$

Figure 6.2.6 Stages in the free-radical substitution of methane with chlorine.

The chlorine radical formed in the second propagation step (Figure 6.2.6) reacts with another methane molecule so the two propagation steps repeat and keep on repeating. This is called a chain reaction and can lead to explosions if chlorine and methane mixtures are exposed to sunlight.

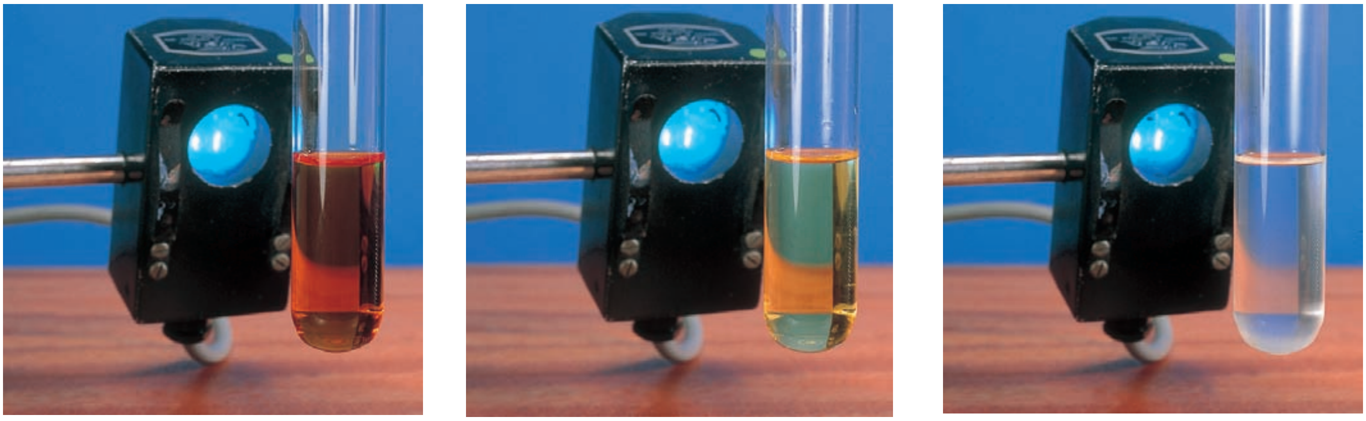
The number of radicals present at any one time is quite small. Each propagation step uses a radical and then forms a radical, so the number of radicals remains fairly constant during the reaction. The likelihood of two radicals colliding is relatively low, so the amount formed of a termination product such as ethane is small. But the fact that any ethane is formed at all confirms that the proposed mechanism is correct.

Tip

Adding the two propagation steps together gives the overall equation for that radical substitution reaction.

In the first propagation step, a chlorine radical extracts a hydrogen atom to form hydrogen chloride. Chloromethane, CH_3Cl, the product of this first substitution, still contains three hydrogen atoms, so further substitution can take place. Further pairs of propagation steps produce dichloromethane, CH_2Cl_2, then trichloromethane, $CHCl_3$, then finally tetrachloromethane, CCl_4, so when chlorine and methane react a mixture of products is formed. To reduce the likelihood of further substitution, an excess of methane can be used but this cannot prevent the formation of a mixture of products. Therefore, radical substitution has limited use in the synthesis of chloroalkanes. Alternative methods of making chloroalkanes are considered in Section 6.3.3.

Other halogen elements such as bromine also react with methane in radical substitution reactions (Figure 6.2.7).



0 s

10 s

16 s

Figure 6.2.7 The effect of light on a mixture of bromine and hexane after 0, 10 and 16 seconds.

Test yourself

4 To what extent is a series of organic compounds, such as the alkanes, comparable to a group of elements in the periodic table?

5 a) Write an equation for the complete combustion of propane in Calor Gas®.

b) What are the products formed when propane burns in a poor supply of oxygen?

c) Why is it important for gas water heaters to be serviced regularly?

6 The boiling temperatures of propane and butane are −42 °C and −0.5 °C respectively. Why is it wise for campers to use Calor Gas® (propane) rather than Gaz® (butane) for cooking during the winter?

7 a) In the substitution of methane with chlorine, chloromethane can be formed both in a propagation step and in a termination step. Write an equation for each step and explain which of the two is more likely.

b) Write an equation for the substitution reaction which occurs when chloromethane reacts with chlorine to form dichloromethane. Write a mechanism for this substitution and label each step.

c) Write overall equations for the two further substitution reactions which occur when dichloromethane reacts with an excess of chlorine and name the products.

d) How could a pure sample of dichloromethane be obtained from the mixture of products formed?

8 a) Why does a mixture of bromine in hexane remain orange in the dark, but fade and become colourless in sunlight?

b) Write an equation for the reaction in part (a).

c) Why can acidic fumes be detected above the solution once the colour has faded?

6.2.4 Fuels from crude oil

Crude oil, also known as petroleum, is arguably the most important naturally occurring raw material. It provides a very large proportion of our energy needs, and is the source of most of our organic chemicals – including plastics, fibres, drugs and pesticides.

Crude oil is a complex mixture of hydrocarbons, most of which are alkanes. Crude oil has no uses in its raw form. The challenge for refineries is to produce the various oil products in the proportions required by industrial and domestic users.

Generally, crude oil contains too much of the high boiling fractions with larger molecules, and not enough of the low boiling fractions with the smaller molecules needed for fuels such as petrol. In order to satisfy the demand for very different products, crude oil undergoes three main processes – fractional distillation, cracking and reforming.

Fractional distillation

Fractional distillation is the first stage in refining crude oil (Figure 6.2.8). This produces fuels and lubricants, as well as feedstocks for the petrochemical industry. The continuous process operates on a large scale, separating crude oil into different fractions.

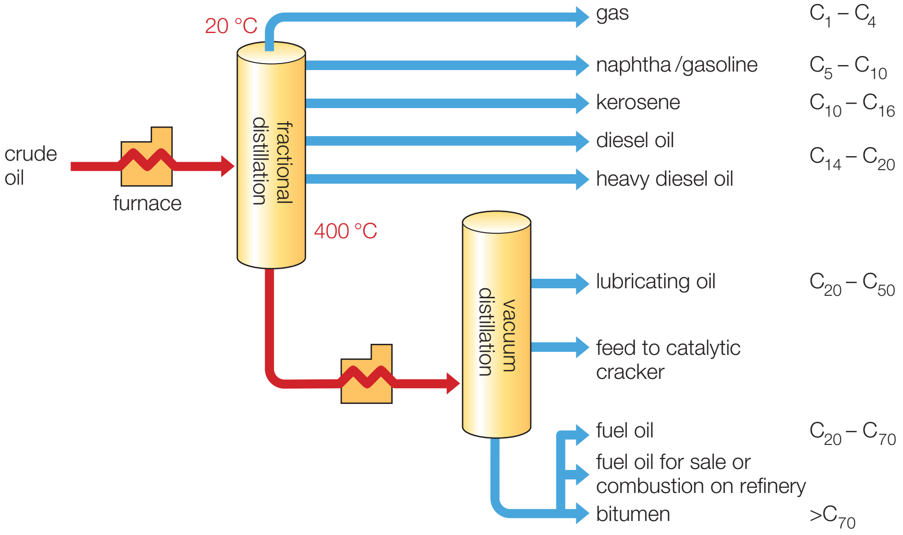

20 °C
gas
$C_1 - C_4$
naphtha /gasoline
$C_5 - C_{10}$
kerosene
$C_{10} - C_{16}$
diesel oil
$C_{14} - C_{20}$
heavy diesel oil
crude oil
furnace
fractional distillation
400 °C
vacuum distillation
lubricating oil
$C_{20} - C_{50}$
feed to catalytic cracker
fuel oil
$C_{20} - C_{70}$
fuel oil for sale or combustion on refinery
bitumen
$>C_{70}$

Figure 6.2.8 The fractional distillation of crude oil.

A furnace heats the crude oil to about 400 °C. The oil then flows into a fractionating tower containing 40 or so horizontal 'trays' pierced with small holes.

The column is hotter at the bottom and cooler at the top. Rising vapour condenses when it reaches the tray with liquid at a temperature just below its boiling temperature. Condensing vapour releases energy. This heats the liquid on the tray and evaporates the more volatile compounds in the mixture on the tray.

With a series of trays, the outcome is that hydrocarbons with small molecules and low boiling temperatures rise to the top of the column, while larger molecules stay at the bottom. Fractions are drawn off from the column at various levels.

Some components of crude oil have boiling temperatures too high for them to vaporise at the furnace temperature and atmospheric pressure. Lowering the pressure in a separate vacuum distillation column reduces the boiling temperatures of these hydrocarbons and this makes it possible to separate them.

Fuel fractions

Petrol is a blend of hydrocarbons based on the gasoline fraction (hydrocarbons with 5–10 carbon atoms), whereas jet fuel is produced from the kerosene (or paraffin) fraction (hydrocarbons with 10–16 carbon atoms). Fuel for diesel engines is made from diesel oil (hydrocarbons with 14–20 carbon atoms).

All these fuels must be refined to remove sulfur compounds, which would cause air pollution when they burn. In addition, petrol must be blended carefully if modern engines are to start reliably and run smoothly (Figure 6.2.9). The proportion of volatile hydrocarbons added to petrol is higher in winter to help cold-starting, but lower in summer to prevent vapour forming too readily.

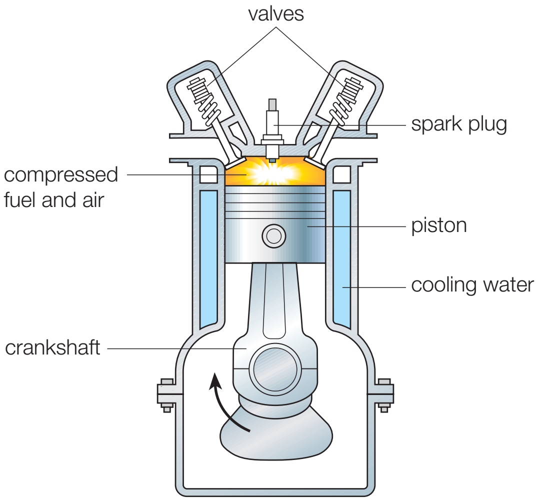


Figure 6.2.9 The working parts of a cylinder in an internal combustion engine that runs on petrol. Sparks from the plugs cause the compressed fuel and air to ignite. This produces more gas molecules, increasing the pressure and forcing the piston down. The product gases are then allowed to escape and, as the pressure falls, the piston rises ready for the next ignition.

For smooth running, petrol must burn smoothly in the engines of vehicles and not in fits and starts. To ensure smooth combustion, companies produce fuel with a high **octane number** by increasing the proportions of branched alkanes and arenes, or blending-in oxygen compounds. The three main methods used to increase the octane number of fuels are:

- *cracking* – which makes smaller molecules and converts straight-chain hydrocarbons to branched and cyclic hydrocarbons
- *reforming* – which turns straight-chain alkanes into branched-chain or cyclic alkanes or arenes such as benzene and methylbenzene and turns cyclic alkanes into arenes

Key term

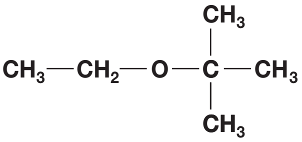
Octane number is a measure of the performance of a fuel by comparison with 2,2,4-trimethylpentane, which is given the number 100, and heptane, which is given the number 0. Most UK petrol has an octane number of 95.

Tip

Straight-chain alkane does not mean literally straight but means unbranched. There are no side chains attached to the carbon skeleton.

The C–C–C bond angles in the carbon skeleton are all about 109.5° (see Section 2.4).

- *adding ethanol and ethers* such as ETBE (initials based on its older name ethyl tertiary butyl ether (Figure 6.2.10). Its correct IUPAC name is 2-ethoxy-2-methylpropane). In the USA and Brazil, a mixture of 10% ethanol and 90% petrol (gasoline), known as gasohol, is commonly used (see Section 6.2.6).



$$CH_3-CH_2-O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

Figure 6.2.10 Structure of the ether ETBE. Adding ETBE is one of the methods used to raise the octane number of gasoline from as low as 70 to 120, the required level for premium petrol.

Cracking

Fractional distillation of crude oil produces a larger supply of the heavier fractions than needed but a lower supply of the fractions most in demand for use as fuels such as petrol. In order to supply more of the smaller molecules, a process called cracking is used to convert heavier fractions, such as diesel oil and fuel oil, into more useful hydrocarbon fuels by breaking up large molecules into smaller ones.

Cracking converts long-chain alkanes with 12 or more carbon atoms into smaller, more useful molecules in a mixture of branched alkanes, cycloalkanes, alkenes and branched alkenes. When conducted at high temperatures in the presence of steam, a higher proportion of alkenes is produced. When conducted in the presence of a catalyst (catalytic cracking), higher yields of branched and cyclic alkanes are produced.

The catalyst is a synthetic sodium aluminium silicate belonging to a class of compounds called 'zeolites'. A zeolite has a three-dimensional structure (Figure 6.2.11) similar in structure to clay, in which the silicon, aluminium and oxygen atoms form tunnels and cavities into which small molecules can fit. Cracking takes place on the surface of the catalyst at about 500 °C.

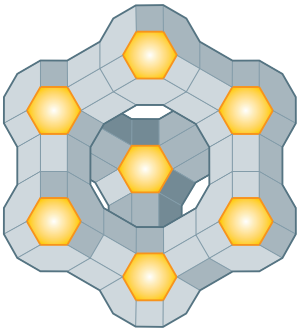


Figure 6.2.11 A model of the structure of a zeolite crystal.

Synthetic zeolites make excellent catalysts because they can be developed with active sites to favour the shapes and sizes of those molecules which react to give the desired products.

Reforming

Reforming converts straight-chain alkanes into branched-chain or cyclic alkanes or arenes such as benzene and methylbenzene, and turns cyclic alkanes into arenes (Figure 6.2.12). Hydrogen is a valuable by-product of the process – it can be used in processes elsewhere at the refinery.

The catalyst for this process is often one or more of the precious metals such as platinum and rhodium supported on an inert material such as aluminium oxide. The process operates at about 500 °C.

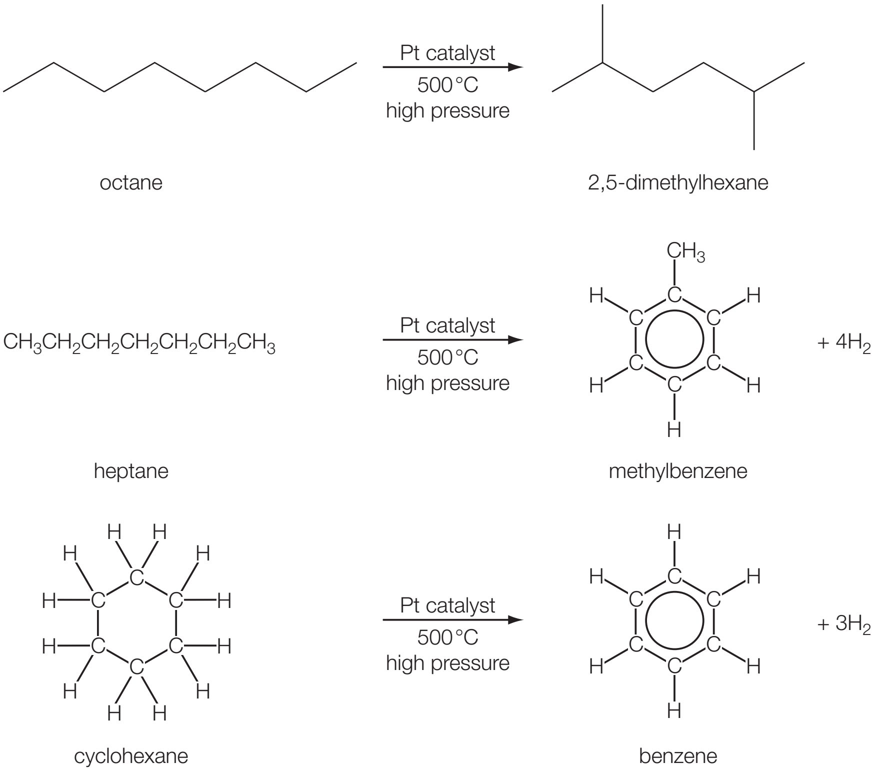


Figure 6.2.12 Examples of reforming.

Test yourself

9 a) Why is crude oil so important?

b) Why should we try to conserve our reserves of crude oil?

10 a) Why do you think that ethanol and ETBE can raise the octane number of petrol?

b) What other methods are used to increase the octane number of petrol?

11 a) Why is cracking important?

b) What conditions are used for catalytic cracking?

12 a) Use displayed formulae to show how catalytic cracking converts hexane into butane and ethene.

b) Use skeletal formulae to show how catalytic cracking converts decane into 2,3-dimethylpentane and propene.

c) Use structural formulae to show how reforming converts hexane into cyclohexane.

d) Use structural formulae to show how reforming converts octane into 1,4-dimethylbenzene and hydrogen.

e) Use molecular formulae to show how an alkane with 16 carbons can be cracked to form molecules of 2,2,4-trimethylpentane, propene and ethene.

6.2.5 Combustion and air pollution

The complete combustion of fuels containing alkanes (Section 6.2.3) provides energy to heat homes and to power vehicles but also releases carbon dioxide into the atmosphere. This carbon dioxide is enhancing the greenhouse effect and is responsible for global warming and climate change. However, motor vehicles and power stations also produce other pollutants during combustion and these can affect the quality of the air we breathe.

Air pollution from motor vehicles

Engines that burn petrol or diesel fuels can pollute the air for three main reasons:

- they do not burn the fuel completely
- the fuel contains impurities
- they run at such a high temperature that nitrogen and oxygen in the air can react.

Although a controlled quantity of air and fuel enters the cylinder of an engine (Figure 6.2.9) before being compressed and burned, some of the fuel may not burn completely and some may not burn at all.

Tip

Oxygen always combines with hydrogen in preference to carbon. So when alkanes are sparked in a limited supply of air, if there is not enough oxygen present to produce water, no combustion occurs at all.

Incomplete combustion

If the supply of air is insufficient, alkanes burn to form water together with either carbon monoxide or carbon.

$$CH_4(g) + 1\tfrac{1}{2}O_2(g) \rightarrow CO(g) + 2H_2O(l)$$

$$C_8H_{18}(l) + 4\tfrac{1}{2}O_{2(g)} \rightarrow 8C(s) + 9H_2O(l)$$

Carbon monoxide is a toxic gas that combines strongly with haemoglobin so that blood can carry less oxygen. In low doses this puts a strain on the heart; in higher doses, it kills.

Tip

PM-10s, Particulate Matter with a diameter of under 10 μm (1 micrometre (μm) = 10^{-6} metre) is of particular concern as it can penetrate so deeply into the lungs. Levels of PM-10s are monitored daily and under European Union air quality laws, levels of PM-10s must not exceed 75 $\mu g\,m^{-3}$ on more than 35 days in a year.

Carbon particles are also produced when combustion is incomplete, especially in diesel engines. The soot formed includes fine particles and nanoparticles which can penetrate deep into the lungs. This causes short-term symptoms such as coughing and headache but long-term exposure is suspected of leading to more serious health problems including heart disease and lung cancer. Modern diesel engines use a diesel particulate filter to capture these carbon particles which are then automatically burned to remove them from the filter.

Unburned hydrocarbons which may enter the atmosphere from incomplete combustion or evaporation of fuel include benzene, which is carcinogenic. Careful monitoring of the air : fuel ratio is used to minimise the release of unused fuel.

Impurities in the fuel

Sulfur compounds are the main impurities in crude oil and must be removed before the petroleum products are used as fuels. This is to ensure that sulfur dioxide emissions are reduced as much as possible as these can lead to acid rain. Removal of sulfur is also necessary to prevent damage which sulfur causes to the catalyst in catalytic converters.

Crude oil is mixed with hydrogen and passed over a hot catalyst. Any sulfur compounds react with hydrogen to form hydrogen sulfide and a hydrocarbon. For instance, ethanethiol, C_2H_5SH, is converted into ethane.

$$C_2H_5SH(l) + H_2(g) \rightarrow C_2H_6(g) + H_2S(g)$$

The hydrogen sulfide produced is then oxidised to sulfur in two steps.

$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$$

$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$$

Huge quantities of sulfur are obtained in this way and most of it is used to make sulfuric acid.

Formation of oxides of nitrogen

When petrol vapour burns in an internal combustion engine, the temperature can rise to 2800 °C. At this temperature, sufficient activation energy is available for nitrogen to react with oxygen and form nitrogen monoxide.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Tip

The same reaction happens during a thunderstorm where lightning provides the energy needed to split nitrogen molecules into atoms. The rain which falls during a thunderstorm is, therefore, a very dilute solution of nitric acid, but it also produces nitrates in the soil and these promote plant growth.

Reaction of NO with more oxygen produces nitrogen dioxide.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

These oxides of nitrogen, NO and NO_2, sometimes referred to as NO_x, react with water and more oxygen to form nitric acid, which leads to the production of acid rain.

$$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(l)$$

In bright sunshine, nitrogen dioxide molecules break down into nitrogen monoxide and oxygen radicals. These oxygen atoms combine with oxygen molecules to form ozone. Ozone itself is a serious pollutant, but it can lead to further harm in still, sunny weather near cities when it mixes with unburned hydrocarbons. The reaction of ozone with hydrocarbons forms a complex mixture of irritant chemicals that in, the absence of any wind, builds up to create a photochemical smog (Figure 6.2.13).

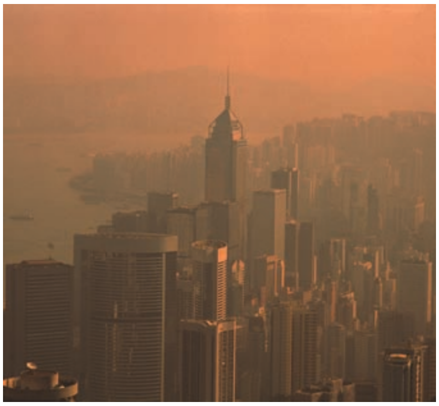


Figure 6.2.13 Photochemical smog over Hong Kong, China.

Catalytic converters

Catalytic converters improve air quality by removing the pollutants that would otherwise be released from car exhausts. In the presence of the catalyst, carbon monoxide and unburned hydrocarbons react with nitrogen oxides to form carbon dioxide and water. The converter contains a honeycomb of ceramic material coated with a thin layer of metals such as rhodium, platinum or palladium. The large surface area increases the rate of reaction (Section 9.4) so that 90% of the pollutant gases are removed in a fraction of a second.

$$2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$$

$$C_8H_{18}(g) + 25NO(g) \rightarrow 8CO_2(g) + 12\tfrac{1}{2}N_2(g) + 9H_2O(g)$$

Tip

These are redox reactions (Section 3.4). In the first example, the toxic reducing agent, CO, is oxidised to CO_2 by a harmful oxidising agent (NO), which is itself reduced to harmless nitrogen.

Test yourself

13 Write equations for:

- **a)** the complete combustion of butane
- **b)** the incomplete combustion of pentane to form only gaseous products
- **c)** the incomplete combustion of hexane to form products which include a solid product
- **d)** the complete combustion of ethanethiol.

14 The flame on a Bunsen burner changes as the air hole is closed. Describe the change and explain why a Bunsen burner should not be used for heating if the air hole is closed.

15 a) Acid rain can contain sulfur compounds or nitrogen compounds. Explain how each type of acid rain is formed.

- **b)** Explain how a catalytic converter removes pollutant gases from car exhaust fumes.

6.2.6 Alternative fuels

Fossil fuels, such as petroleum and natural gas, were formed millions of years ago by the anaerobic decomposition of remains of organisms that settled at the bottom of the sea. These fuels are considered to be non-renewable because supplies of them are being consumed at a much faster rate than they are being replenished. Therefore, supplies of fossil fuels will eventually run out and alternative supplies of energy must be used to provide the world's energy needs.

The combustion of fossil fuels produces carbon dioxide, so concerns both about supplies of fossil fuels and also the enhanced greenhouse effect are encouraging people and governments to reduce their CO_2 emissions and seek a more sustainable development. This involves planning to live within the means of the environment in order that the Earth's natural resources are not destroyed, but remain available for future generations.

Any attempt to reduce CO_2 emissions means seeking alternatives to fossil fuels. These alternatives include nuclear, solar, wind and wave power, but also include renewable energy supplies such as biofuels – bioethanol and biodiesel.

Crops take in carbon dioxide from the air as they photosynthesise, making sugars and vegetable oils that can be used to produce biofuels. When the biofuels burn, the carbon dioxide that is taken up during photosynthesis is returned to the air. This analysis suggests that the use of biofuels should have no overall effect on the level of carbon dioxide in the atmosphere. Because of this, biofuels are sometimes described as **carbon neutral**.

However, this analysis ignores the carbon dioxide released from fossil fuels during the mechanical planting, harvesting and processing of the crop, and in the manufacture of fertilisers applied to the crop during the growing season.

Key term

A process is termed **carbon neutral** if the carbon dioxide (or other greenhouse gases) released is balanced by actions which remove an equivalent amount of carbon dioxide from the atmosphere.

The principal biofuels now being used are bioethanol and biodiesel. Bioethanol is manufactured by fermenting carbohydrates such as starch and sugar in crops like sugar cane. Countries, such as Brazil, with limited natural oil supplies use fuels consisting of bioethanol on its own or in mixtures (Figure 6.2.14).

Fermentation converts starch to glucose, and then glucose to ethanol and carbon dioxide. The process is catalysed by enzymes in yeast.

$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \rightarrow \underset{\text{carbon dioxide}}{2CO_2(g)} + \underset{\text{ethanol}}{2C_2H_5OH(aq)}$$

Biodiesel is produced by extracting and processing the oils from crops such as rapeseed.

Studies of the overall impact of biofuels have produced conflicting results. Some have even suggested that more energy is expended in making the bioethanol than is available from burning the fuel. A more optimistic study has suggested that ethanol from maize in the USA does reduce greenhouse gas emissions, but only by about 12% compared to petrol.

Reduction in CO_2 emissions is more favourable for biodiesel from vegetable oil. Biodiesel from soya beans can reduce emissions by 41% compared with conventional diesel fuel. This is mainly because energy is not needed for distillation during the production of the fuel. In addition, far fewer fertilisers and pesticides are used in growing soya beans.

Instead of making bioethanol from maize, a better solution is to produce ethanol from non-food sources, such as woody plants and agricultural wastes including straw. Using micro-organisms to break down cellulose to sugars does not compete with food supplies and makes it possible to process large amounts of waste. However, this approach is still at the research and development stage.

The conditions for producing bioethanol in Brazil are more favourable. The ethanol is manufactured by fermenting sugars from sugar cane. The refineries that make bioethanol in Brazil have the advantage that they can meet all their energy needs for heating and electricity by burning the sugar-cane waste. However, there are several negative aspects of this industry in Brazil where, among other things, large-scale deforestation has been carried out to make way for sugar cane plantations. Also, when land use is switched from food crops to biofuel crops, food prices rise and food production is displaced. This causes cropland expansion elsewhere, threatening tropical forests and causing loss of biodiversity.

ALCOOL Comum
GASOLINA Comum
1 2 9 9
2 3 4 9

Figure 6.2.14 Brazil is the leading country to use bioethanol. This photo shows a petrol station in São Paulo. The ethanol fuel ('álcool') is cheaper than the petrol ('gasolina').

Test yourself

16 Why are governments around the world becoming increasingly concerned about our use of fossil fuels and the need for sustainable development?

17 Suggest three ways in which our use of fossil fuels might be reduced.

18 Biofuels are sometimes described as 'carbon neutral'. Why is this and to what extent is it true?

19 Why does the use of bioethanol in Brazil have a smaller carbon footprint compared to the use of bioethanol in the USA?

6.2.7 Alkenes

The alkenes form a series of organic compounds in which the functional group is a carbon–carbon double bond, C=C. Because of this, their molecules have two atoms of hydrogen fewer than the corresponding alkane, and their general formula is C_nH_{2n}. As they have less than the maximum content of hydrogen, they are described as being **unsaturated**. The term is applied to alkenes and also used describe unsaturated fats which have C=C double bonds in their hydrocarbon chains.

Key term

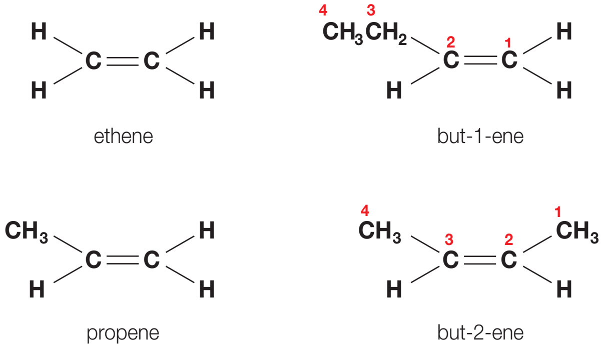
Unsaturated compounds contain one or more double or triple bonds between atoms in their molecules.

Tip

The general formula C_nH_{2n} applies to cyclic alkanes as well as alkenes. Both types of hydrocarbon have two hydrogen atoms fewer than the corresponding alkane.

Names and structures

The name of an alkene is based on the name of the corresponding alkane with the ending -ene in place of -ane (Figure 6.2.15).



ethene

but-1-ene

propene

but-2-ene

Figure 6.2.15 The names and structures of the four simplest alkenes.

Where necessary, a number in the name shows the position of the double bond, as in the structural isomers but-1-ene and but-2-ene. Counting starts from the end of the chain that gives the lowest possible number in the name. This number indicates the first of the two atoms connected by the double bond. In but-1-ene, for example, the double bond is between carbon atoms numbered 1 and 2.

Physical properties

Like the alkanes, the melting and boiling temperatures of alkenes increase as the number of carbon atoms in the molecules increases. Ethene, propene and the butenes are gases at room temperature. Alkenes, like other hydrocarbons, do not mix with or dissolve in water.

The double bond in alkenes

Chemists have extended the theory of atomic orbitals (Section 1.6) to describe the distribution of electrons in molecules. This molecular orbital theory is helpful in discussing the bonding and reactivity of alkenes.

Molecular orbitals result when atomic orbitals overlap, forming bonds between atoms. The shape of a molecular orbital shows the regions in space where there is a high probability of finding electrons. A sigma (σ) bond is a single covalent bond formed by a pair of electrons in an orbital in a molecule with the electron density concentrated between two nuclei. Free rotation is possible around single bonds.

Sigma bonds can form by the overlap of two s orbitals, an s orbital and a p orbital, or two p orbitals (Figure 6.2.16).

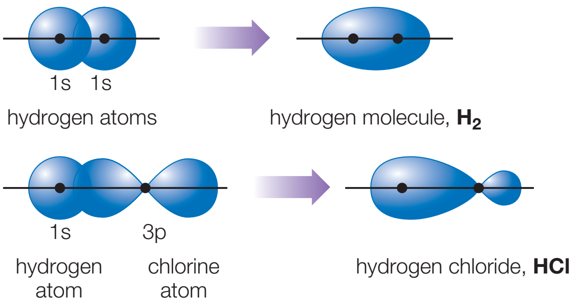


Figure 6.2.16 Examples of sigma bonds in molecules.

A pi (π) bond is the type of bond found in molecules with double and triple bonds. The bonding electrons are in a π orbital formed by the *sideways overlap* of two atomic p orbitals. In a π bond, the electron density is concentrated in two regions – one above and the other below the plane of the molecule, on either side of the line between the nuclei of the two atoms joined by the bond (Figure 6.2.17). Rotation around a double bond is restricted because of these regions of high electron density.

Tip

In order for a π bond to form, two atomic p orbitals must overlap sideways. If there is any rotation of the carbon–carbon bond, the p orbitals can no longer overlap sideways.

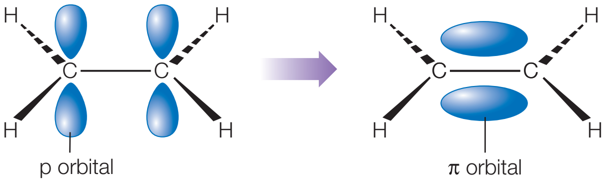


Figure 6.2.17 The π bond in ethene.

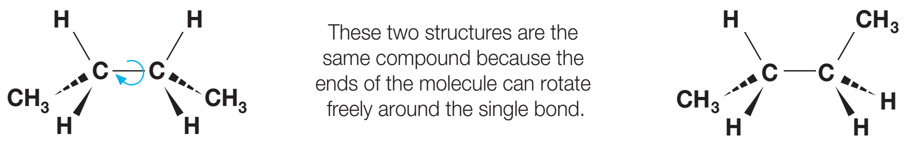
6.2.8 *E/Z* isomerism

X-ray diffraction studies show that the ethene molecule is planar (Figure 6.2.15) with the three atoms around each carbon atom arranged trigonally at approximately 120°. However, the CH_2 groups in ethene cannot be rotated around the carbon–carbon double bond. In ethane and other alkanes, it is possible to rotate the whole molecule around a single σ bond, because this does not affect the overlap of orbitals (Figure 6.2.18). But with a double bond, rotation would involve breaking the π bond and this requires more energy than the molecules possess at normal temperatures. So, free rotation is not possible around the carbon–carbon double bond in alkenes and this gives rise to ***E/Z* isomerism**, which is a form of **stereoisomerism**.

Key terms

***E/Z* isomerism** occurs where there is restricted rotation about a bond and also different groups are attached to the carbon atoms at each end of the bond.

Stereoisomerism occurs when molecules with the same molecular formula and the same structural formula have a different spatial arrangement of bonds.



These two structures are the same compound because the ends of the molecule can rotate freely around the single bond.

Figure 6.2.18 Free rotation can occur around a single σ bond.

E/Z isomerism involves molecules with

- restricted rotation about a bond
- different groups attached to the carbon atoms at each end of the bond.

Restricted rotation usually involves C=C double bonds but can also involve single bonds in cyclic compounds (see the Activity on page 186).

Activity

Renaming *cis–trans* as *E/Z* isomers

Cis–trans isomerism arises in compounds containing carbon–carbon double bonds when there are two different groups on both carbon atoms of the double bond. Different isomers result because of restricted rotation around the double bond.

The existence of a ring structure in a molecule can also restrict rotation and give rise to *cis* and *trans* isomers. Look at the structure of *trans*-1,2-dichlorocyclobutane in Figure 6.2.19. Its *cis* isomer is *cis*-1,2-dichlorocyclobutane.

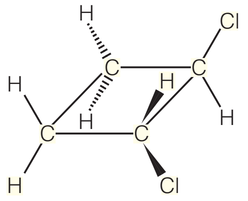


Figure 6.2.19 The structure of *trans*-1,2-dichlorocyclobutane.

1 Draw the displayed formula of *cis*-1,2-dichlorocyclobutane.
2 There is another pair of *cis–trans* isomers named dichlorocyclobutane and a separate structural isomer. Name and draw displayed formulae for these three molecules.

Now look at the isomer of 2-bromo-1-chloroprop-1-ene in Figure 6.2.20.

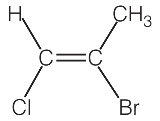


Figure 6.2.20 An isomer of 2-bromo-1-chloroprop-1-ene.

3 Draw the other *cis–trans* isomer of 2-bromo-1-chloroprop-1-ene.

But, which of these isomers is *cis* and which is *trans*? The rule normally used to name the isomers as *cis* or *trans* is:

- in the *cis* isomer, similar groups are on the same side of the double bond
- in the *trans* isomer, similar groups are on opposite sides of the double bond.

In 2-bromo-1-chloroprop-1-ene, there are four different groups on the atoms joined by the double bond. So the normal rule, which requires one group to be the same on both carbon atoms, cannot be used. This is where the *cis–trans* naming system breaks down and it becomes necessary to use the *E/Z* naming system. In fact, the *E/Z* naming system was developed in order to name complex alkenes in naturally occurring materials, such as the red pigment in tomatoes. One molecule of this pigment has 13 C=C bonds.

The *E/Z* naming system

- Look at the atoms bonded to the first carbon atom in the C=C bond. The atom with the highest atomic number takes priority.
- If two atoms with the same atomic number, but in different groups, are attached to the first carbon atom, then the next bonded atom is taken into account. Thus, CH_3CH_2- has priority over CH_3-.
- This consideration is then repeated with the second carbon atom in the C=C bond.

4 **a)** What is the order of priority among Br, C in CH_3, Cl and H?
  b) What is the priority among CH_3-, CH_3CH_2-, CH_3O- and $HOCH_2-$?

5 Look again at 2-bromo-1-chloroprop-1-ene in Figure 6.2.20.
  a) What is the priority between H– and Cl– attached to the first carbon atom in the double bond?
  b) What is the priority between Br– and CH_3- attached to the second carbon atom in the double bond?

If the two groups of highest priority are on the same side of the double bond, the isomer is designated *Z*- (from the German ‘*zusammen*’ meaning ‘together’), and if the two groups of highest priority are on opposite sides of the double bond, the isomer is designated *E*- (from the German ‘*entgegen*’ meaning ‘opposite’).

6 Draw the displayed structure of *Z*-2-bromo-1-chloroprop-1-ene.
7 Use the *E/Z* system to name the *cis* and *trans* isomers of:
  a) but-2-ene
  b) 1,2-dichlorocyclobutane.
8 Name the two compounds in Figure 6.2.21 using the *cis–trans* system and also using *E/Z*. Comment on your answers.

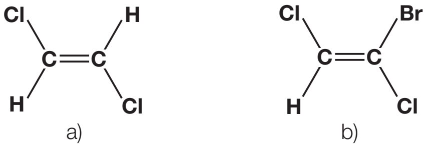
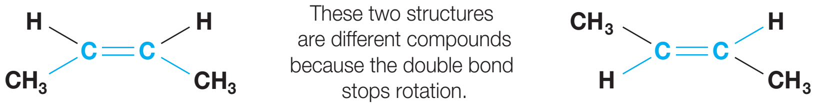


Figure 6.2.21

The simplest type of *E*/*Z* isomerism occurs when at least one group on each carbon is the same. This is called *cis-trans* isomerism.

In the *cis* isomer, similar groups are on the same side of the double bond (in Latin, *cis* means 'on the same side'). In the *trans* isomer, similar groups are on opposite sides of the double bond (in Latin, *trans* means 'opposite' or 'across'). But-2-ene can exist as a *cis* isomer where the methyl groups are on the same side or a *trans* isomer where the methyl groups are on opposite sides (Figure 6.2.22).



These two structures are different compounds because the double bond stops rotation.

melting temperature = −139 °C
cis-but-2-ene

melting temperature = −106 °C
trans-but-2-ene

Figure 6.2.22 *Cis* and *trans* isomers of but-2-ene – different compounds with different melting temperatures, boiling temperatures and densities.

Naming isomers becomes more complicated for examples such as 2-bromo-1-chloroprop-1-ene (Figure 6.2.20), where no substituents on the double bond are the same. For these molecules it is necessary to use the *E*/*Z* naming system (see Activity: Renaming *cis*–*trans* as *E*/*Z* isomers).

Test yourself

20 Why do you think the bond angles around each carbon atom in ethene are approximately 120°?

21 Why is rotation about a carbon–carbon double bond restricted?

22 Which of the following unsaturated compounds have *cis–trans* isomers: but-1-ene, 1,1-dichloropropene, pent-2-ene, buta-1,3-diene?

23 **a)** Draw and name the displayed structures of the three isomers of $C_2H_2Br_2$.

b) What types of isomerism do they show?

6.2.9 Chemical reactions of the alkenes

Combustion

Alkenes are hydrocarbons so like alkanes will burn in air and oxygen. The flame when an alkene burns is more smoky than that of an alkane with the same number of carbon atoms because the alkene contains a higher percentage of carbon.

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \qquad \Delta_c H^{\ominus} = -1411\ \text{kJ mol}^{-1}$$

Alkenes are rarely burned as fuels because they react in other more useful ways. The characteristic reactions of alkenes are addition reactions (Section 6.1.6), in which small molecules such as H_2, Cl_2 and HBr add across the double bond to form a single product.

Tip

When describing an organic reaction, always write an equation, name the reagents and the products, and state the conditions (temperature, pressure, catalysts).

Addition of hydrogen

Hydrogen adds to C=C double bonds in alkenes such as propene at room temperature in the presence of a platinum or palladium catalyst, or on heating to 150 °C in the presence of a nickel catalyst (Figure 6.2.23).

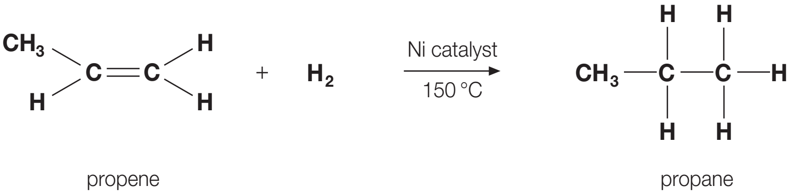


Figure 6.2.23 Addition of hydrogen to propene.

This process is known as 'catalytic hydrogenation' and is used in the manufacture of margarine from unsaturated vegetable oils in palm seeds and sunflower seeds. The advantage of using a solid metal catalyst is that it can be held in the reaction vessel as the reactants flow in and the products flow out. There is no difficulty in separating the products from the catalyst.

Vegetable oils are liquids containing carbon–carbon double bonds, nearly all of which are *cis*-double bonds. During hydrogenation, some of these double bonds are converted to carbon–carbon single bonds by addition of hydrogen. The change in structure turns oily unsaturated liquids into soft saturated fatty solids like margarine. However, research in the 1960s started to show that saturated fats contribute to heart disease.

Fats that have been partially saturated by hydrogenation often contain *trans*-fats and, during the 1990s, evidence began to suggest that these *trans*-fats could also lead to high cholesterol levels in the blood and so also cause heart disease. In some parts of the world, *trans*-fats such as *E*-octadec-9-enoic acid (Figure 6.2.24) were banned by law. Elsewhere manufacturers of margarine and vegetable fat spreads agreed voluntarily to remove artificial *trans*-fats from their products. In UK, the agreed date for their removal was the end of 2012. A new strategy adopted by the manufacturers is to hydrogenate a proportion of the vegetable oils completely. This removes all the double bonds, hence the *trans*-fats. They then blend this product with untreated oil to make a spread of the correct texture, but with no *trans*-fats (Figure 6.2.25).

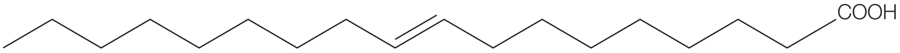


Figure 6.2.24 *E*-octadec-9-enoic acid is the main *trans*-fat found in hydrogenated vegetable oils.

BERTOLLI
BERTOLLI
Olive Oil
goodness for a healthy lifestyle

Figure 6.2.25 Manufacturers of vegetable fat spreads, such as Bertolli, often claim that their products contain virtually no *trans*-fats, and that they are rich in unsaturated fat and low in saturated fats compared to butter. These spreads are claimed to be a healthier option than butter.

Addition of halogens

Chlorine and bromine add rapidly to alkenes at room temperature (Figure 6.2.26). The products are dichloroalkanes and dibromoalkanes and the reaction proceeds by an electrophilic addition mechanism (Section 6.2.10). Fluorine reacts explosively with small alkenes, such as ethene and propene, but the reaction of iodine with alkenes is slow.

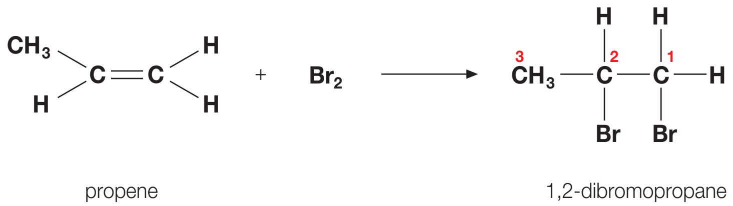


Figure 6.2.26 Addition of bromine to propene.

Tip

The reaction of bromine water (aqueous bromine, $Br_2(aq)$) with hydrocarbons is a useful test for alkenes and the carbon–carbon double bond.

Unsaturated hydrocarbons with a C=C bond, such as ethene and cyclohexene, quickly decolorise yellow/orange bromine water, producing a colourless mixture (see Section 6.2.10).

Saturated hydrocarbons, such as ethane and cyclohexane, have no reaction with bromine water and the yellow/orange colour of bromine remains.

Addition of hydrogen halides

Hydrogen halides react readily with alkenes at room temperature, forming halogenoalkanes. For example, hydrogen bromide reacts with ethene in the gas phase to form bromoethane (Figure 6.2.27). The reaction follows an electrophilic addition mechanism (Section 6.2.10).

The other hydrogen halides, HCl and HI, react in a similar way.

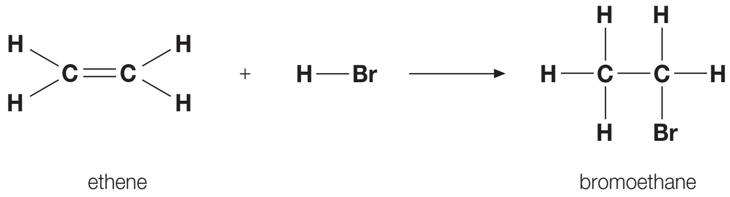


Figure 6.2.27 Addition of hydrogen bromide to ethene.

Addition of steam

Alkenes react with steam in the presence of an acid catalyst to produce alcohols. The direct catalytic hydration of ethene, for example, produces ethanol in a reversible reaction between ethene and steam (Figure 6.2.28).

The phosphoric acid catalyst is adsorbed on silica and the conditions used are 570 K and a pressure of 6.5 MPa (65 atmospheres) (see Section 10.4 Activity: The manufacture of ethanol).

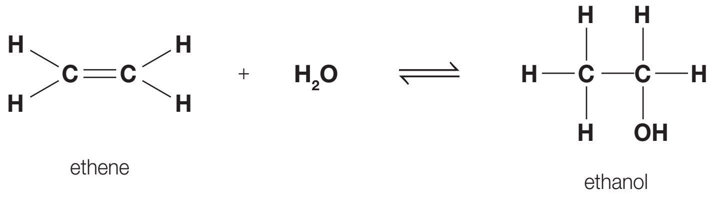


Figure 6.2.28 Hydration of ethene to produce ethanol.

Oxidation by potassium manganate(VII)

Potassium manganate(VII) oxidises alkenes – the products depend on the conditions. A dilute, acidified solution of potassium manganate(VII) converts an alkene to a diol at room temperature (Figure 6.2.29). At the same time, purple manganate(VII) ions, MnO_4^-, are reduced to very pale pink Mn^{2+} ions, and the purple colour disappears if there is excess alkene. So, like the reaction with aqueous bromine (Section 6.2.10), this reaction with dilute acidified potassium manganate(VII) solution can be used to distinguish between unsaturated and saturated hydrocarbons.

Tip

The symbol [O] represents the oxidising agent and can be used in simplified equations for such reactions. The mechanism for this reaction is not required at A Level.

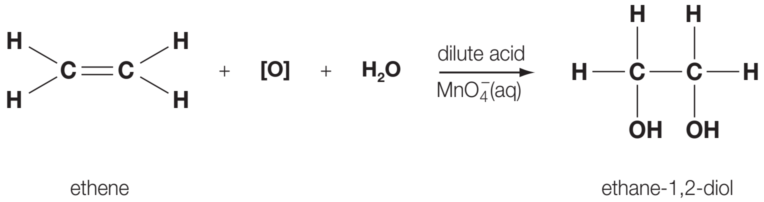


Figure 6.2.29 The reaction of ethene with dilute acidified manganate(VII) ions producing ethane-1,2-diol.

Test yourself

24 **a)** Write the structures and names of the products and the conditions for the reactions when propene reacts with:

- **i)** hydrogen
- **ii)** chlorine.

b) Write the structures and names of the products and the conditions for the reactions when but-2-ene reacts with:

- **i)** hydrogen chloride
- **ii)** steam.

25 State what you would see when a few cm^3 of acidified potassium manganate(VII) solution is added to a gas jar of propene and the mixture is shaken. Write an equation for the reaction and name the product.

26 Catalytic hydrogenation is sometimes used in the manufacture of spreads, such as 'Flora™', from vegetable oils.

a) What is meant by the term 'catalytic hydrogenation'?

b) Explain the terms 'saturated' and 'unsaturated' as applied to organic compounds such as those in low-fat spreads and vegetable oils.

c) Why are some unsaturated fats, such as olive oil and sunflower oil, thought to be healthier foods than more saturated fats, such as cream, and which type of unsaturated fats are now known to be unhealthy?

6.2.10 Mechanism for electrophilic addition to alkenes

Most of the reactions of alkenes are electrophilic addition reactions. Electrophiles (Section 6.1.7) attack the electron-rich region of the double bond in alkenes and, in particular, the exposed π bond. Electrophiles that add to alkenes include hydrogen bromide, bromine and water in the presence of H^+ ions.

The addition of hydrogen bromide to ethene

Hydrogen bromide molecules are polar (Section 2.5). The hydrogen atom, with its $\delta+$ charge at one end of the molecule, acts as an electrophile (Figure 6.2.30).

Tip

The $\delta+$ hydrogen in HBr acts as an electrophile. Because of the electron-rich double bond, ethene donates a pair of electrons and so acts as a nucleophile. The reaction, however, is always described as electrophilic addition of the inorganic species to the organic compound.

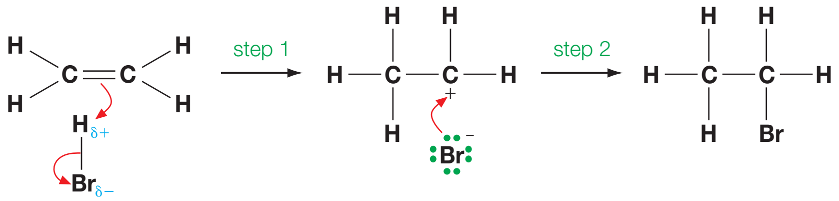


Figure 6.2.30 Electrophilic addition of hydrogen bromide to ethene. The reaction takes place in two steps.

In the first step of the reaction, an HBr molecule approaches an ethene molecule. The $\delta+$ hydrogen end of the HBr is attracted towards the electron-rich double bond. As the HBr molecule gets even closer, heterolytic fission of the π bond occurs. The electrons in the π bond form a covalent bond to the hydrogen atom and, at the same time, heterolytic fission of the HBr bond also occurs. Electrons in the H–Br bond are taken over by the bromine atom, producing a Br^- ion.

Tip

A curly arrow represents the movement of a pair of electrons. In step 1 each curly arrow starts from the bond that is breaking.

In step 2, the curly arrow starts from a lone pair on the bromide ion.

The other product of step 1 is the highly reactive **carbocation** $CH_3CH_2^+$. This reacts immediately with the bromide ion; a pair of electrons from Br^- is used to form a covalent bond with the electron-deficient carbon of the carbocation. This rapid second step forms bromoethane, CH_3CH_2Br.

Key term

A **carbocation** is a reactive species which contains a carbon atom which has a positive charge.

The addition of bromine to ethene

The addition of bromine to ethene is also an electrophilic addition. Bromine molecules are not polar, but they become polarised as they approach the electron-rich region of the double bond. Electrons in the double bond repel electrons in the bromine molecule, so the end of the bromine molecule (nearer the double bond) becomes $\delta+$ and electrophilic (Figure 6.2.31). In this case, the product is 1,2-dibromoethane.

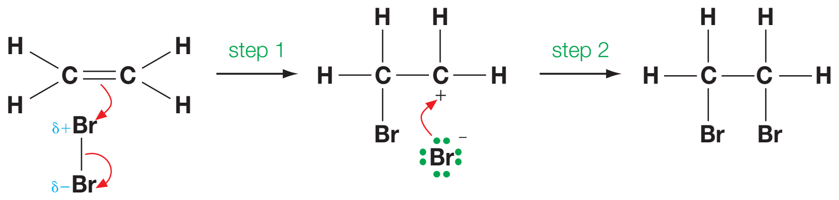


Figure 6.2.31 Electrophilic addition of bromine to ethene.

Tip

Always show relevant dipoles in these mechanisms to make it clear that the electrophilic $\delta+$ end of a molecule is attracted to the electron-rich double bond.

The reaction of bromine water (aqueous bromine, $Br_2(aq)$) with hydrocarbons is a useful test for alkenes (see Section 6.2.9).

When bromine water is shaken with ethene, bromine molecules react with the electron-rich region of the C=C bond forming an intermediate carbocation, the same as with liquid bromine. But in aqueous solution, this carbocation can react either with Br^- ions or with water molecules in the bromine water to form a mixture of 1,2-dibromoethane and 2-bromoethanol

(Figure 6.2.32). There are many more water molecules than bromide ions present, so water molecules are more likely to collide with the carbocation. The major product of the reaction of ethene with bromine water is, therefore, 2-bromoethanol.

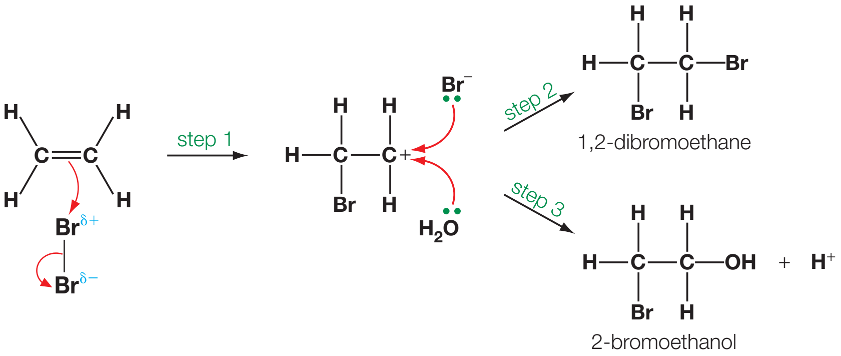


Figure 6.2.32 Reaction of bromine water with ethene producing 1,2-dibromoethane and 2-bromoethanol.

When bromine is added to water, some of it reacts with the water to form a mixture of hydrobromic acid and bromic(I) acid. Hydrobromic acid is a strong acid and ionises immediately. In comparison, bromic(I) acid is a weak acid which remains un-ionised as polar $HO^{\delta-}-Br^{\delta+}$ molecules.

$$Br_2(l) + H_2O(l) \rightleftharpoons H^+(aq) + Br^-(aq) + HOBr(aq)$$

The reaction of ethene with bromine water can be represented by the addition of HOBr to ethene (Figure 6.2.33).

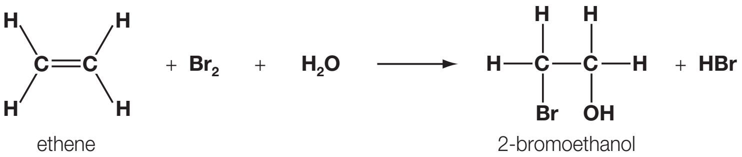


Figure 6.2.33 Formation of 2-bromoethanol when bromine water reacts with ethene.

These mechanisms for electrophilic additions are not simply hypotheses or good ideas. They are supported by significant experimental evidence to help our understanding of the reactions at a molecular level. This evidence includes data from studies of the kinetics of the reactions, as well as the structures of the products formed. For instance, if the addition of HBr is carried out in the presence of NaCl then, in addition to the expected product, CH_3CH_2Br, some chloroethane, CH_3CH_2Cl, is also obtained. Similarly, if the addition of Br_2 is carried out in the presence of NaCl then 1-bromo-2-chloroethane, CH_2BrCH_2Cl, is obtained as well as CH_2BrCH_2Br.

The formation of these extra products can only be explained using the two-step mechanism proposed. The highly reactive carbocations $CH_3CH_2^+$ and $CH_2BrCH_2^+$ formed during the slow first step can be attacked either by Br^- or Cl^- ions in the rapid second step of the mechanism, so two products are formed.

6.2.11 Addition to unsymmetrical alkenes

When a molecule such as HBr or HCl adds to an unsymmetrical alkene, such as propene, there are two possible products. Although it might be expected that equal amounts of both products would be formed, in fact much more of one product is usually produced (Figure 6.2.34).

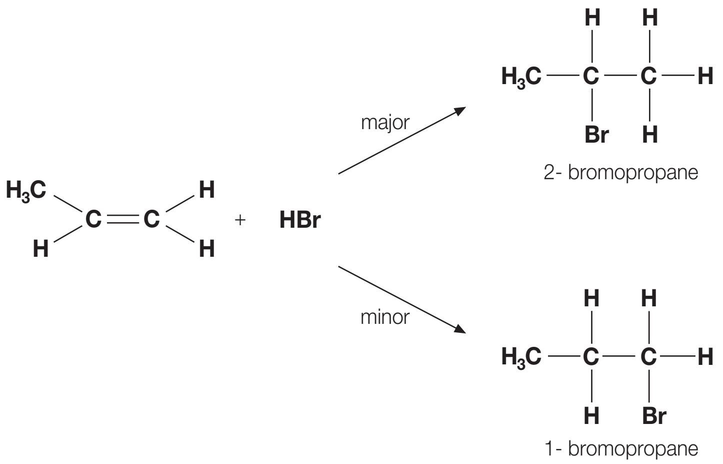


Figure 6.2.34 Possible products when hydrogen bromide adds to propene.

Analysis of the products of the reaction between hydrogen bromide and propene shows that much more 2-bromopropane is produced than 1-bromopropane. This suggests that the hydrogen atom from HBr adds mainly to the carbon atom of the double bond which already has more hydrogen atoms attached to it. This pattern is usually called Markovnikov's rule because it was first reported by the Russian chemist Vladimir Markovnikov who studied many alkene addition reactions during the 1860s.

Modern theories can explain which of the two products is more likely to form by considering the mechanism of the reaction and the relative stability of the **intermediates** (carbocations) formed.

The stability of a carbocation depends on the number of alkyl groups attached, because these alkyl groups exert an **inductive effect** on the carbocation.

Alkyl groups have a small tendency to push electrons towards any carbon atom to which they are bonded; they are said to have a positive inductive effect.

One consequence of this is that any carbon atom with a positive charge is more stable the more alkyl groups are attached to it.

A **primary** carbocation has one alkyl group attached to C+.

A **secondary** carbocation has two alkyl groups attached to C+ and is more stable than a primary carbocation.

A **tertiary** carbocation has three alkyl groups attached to C+ and is more stable than a secondary or a primary carbocation.

Key terms

Intermediates are atoms, molecules, ions or free-radicals which do not appear in the overall equation for a reaction, but which are formed during one step of a reaction and then used up in the next.

The **inductive effect** describes the way in which electrons are either pushed towards or pulled away from a carbon atom by the atoms or groups to which it is bonded.

A **primary** carbon is attached to one other carbon. A **secondary** carbon is attached to two others. A **tertiary** carbon is attached to three others.

Figure 6.2.35 shows the possible carbocation structures of $C_4H_9^+$ and their relative stabilities.

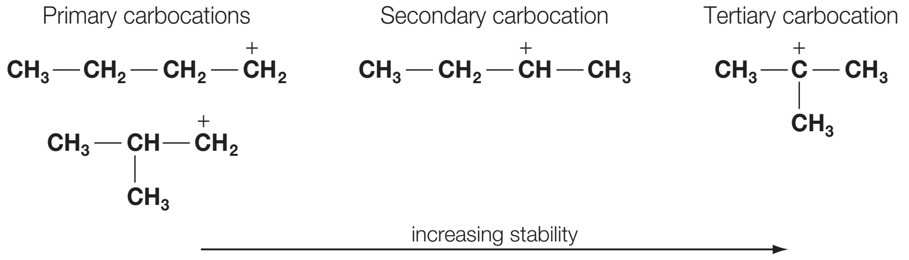

Primary carbocations
$CH_3—CH_2—CH_2—\overset{+}{C}H_2$
$CH_3—CH—\overset{+}{C}H_2$
CH_3
Secondary carbocation
$CH_3—CH_2—\overset{+}{C}H—CH_3$
Tertiary carbocation
$CH_3—\overset{+}{C}—CH_3$
CH_3
increasing stability

Figure 6.2.35 Isomeric primary, secondary and tertiary carbocations, $C_4H_9^+$.

Tip

Halogen atoms are very electronegative and draw electrons in a bond to themselves; halogen atoms are said to have a negative inductive effect.

In the mechanism for electrophilic addition of HBr to propene, there are two possible carbocation intermediates (Figure 6.2.36).

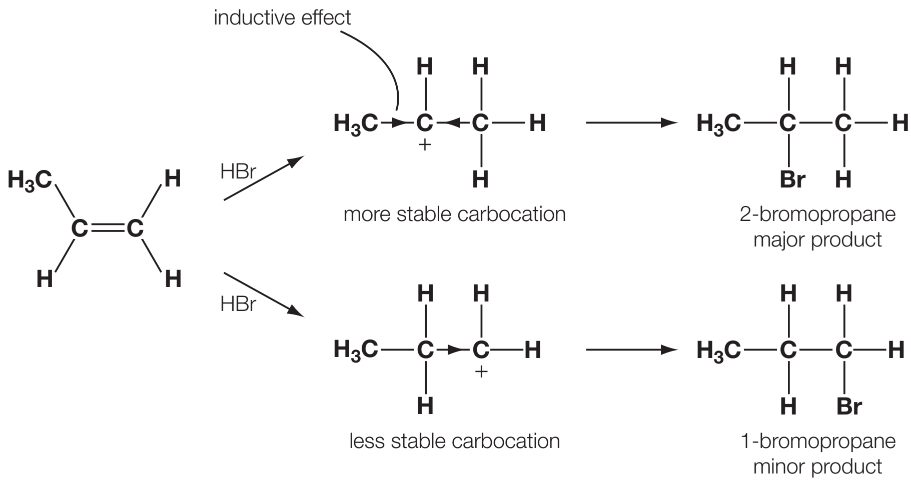

inductive effect
HBr
HBr
more stable carbocation
2-bromopropane
major product
less stable carbocation
1-bromopropane
minor product

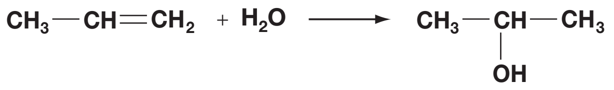
Figure 6.2.36 The formation of primary and secondary carbocations in the reaction of propene with HBr.

The secondary carbocation with its positive charge in the middle of the carbon chain is slightly more stable than the primary carbocation with its charge at the end of the chain. The secondary carbocation has two alkyl groups pushing electrons towards the positively charged carbon atom. By contrast, the primary carbocation only has one alkyl group pushing electrons. This extra inductive effect helps to stabilise the secondary ion slightly more by reducing its positive charge. Because of this extra stability, the secondary carbocation is more likely to form. Subsequent rapid attack by bromide ions then leads to the formation of the major product, 2-bromopropane.

Tip

The stability of a carbocation depends on the *number* of alkyl groups attached and not on the *size* of the alkyl group.

All electrophilic additions proceed via carbocation intermediates, so major and minor products will be formed where the alkene and the molecule added are both unsymmetrical. For instance, the hydration of propene produces propan-2-ol as the major product (Figure 6.2.37). Propan-2-ol is used as a solvent and also used to make propanone, an important compound in the plastics industry.



$$CH_3—CH{=}CH_2 + H_2O \longrightarrow CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$$

Figure 6.2.37 The hydration of propene to form propan-2-ol.

Test yourself

27 **a)** Draw a mechanism for the reaction of bromine with but-2-ene and name the product.

b) Write an equation for the reaction of bromine water with but-2-ene showing the structure of the major product. Explain why this product is different from that obtained in part (a).

28 Consider the reactions of:

a) hydrogen chloride with but-1-ene

b) hydrogen bromide with 2-methylpropene.

In each case:

i) draw the structure of the two possible carbocation intermediates

ii) explain which carbocation is the more stable

iii) write the displayed formula and name of the major product.

29 When propene reacts with bromine in the presence of sodium chloride, a mixture of products is formed. Explain why the mixture contains:

a) more 1-bromo-2-chloropropane than 2-bromo-1-chloropropane

b) 1,2-dibromopropane but not 1,2-dichloropropane.

6.2.12 Addition polymers from alkenes

If the conditions are right, molecules of ethene undergo addition reactions with each other to form polythene – or more correctly, poly(ethene). Two different kinds of polythene are manufactured – low-density polythene and high-density polythene.

Low-density polythene (LDPE) is manufactured by heating ethene at high pressures and high temperatures with special substances called initiators. These initiators are often peroxides. The weak O−O single bond easily breaks homolytically to form free radicals that initiate (start) the reaction (Figure 6.2.38). After this initiation step, the polymerisation proceeds in a series of propagation steps: a radical reacts with ethene and a new radical is formed in each step. The polymer chain grows stepwise until termination steps occur. The polyethene produced has very long chains but it also has lots of branches (which result from complex collisions between radicals). The branches prevent the molecules from packing closely and this results in low-density material.

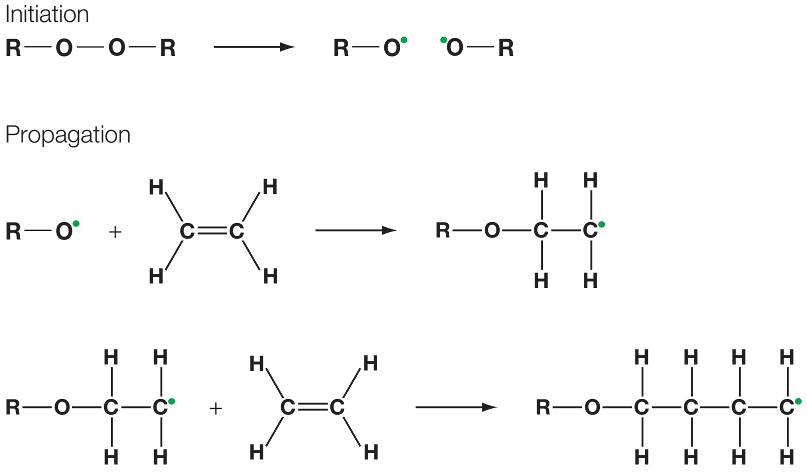


Figure 6.2.38 Molecules of ethene can undergo stepwise addition reactions with each other.

Activity

A more sustainable future for polymers

Manufactured goods, such as polymers, are produced at a heavy cost to society and the environment. In general, their production uses up scarce natural resources, consumes non-renewable fuels and energy, and disrupts wildlife and the countryside.

Today's industrialists and manufacturers are expected to assess the life cycles of their products more closely, in order to find ways in which industry and society can contribute to a more sustainable use of materials. This life cycle assessment (LCA) is part of the legislation designed to protect the environment.

In terms of energy and materials, manufactured goods such as computers, clothes and cars go through a life cycle with three distinct phases:

- *birth* – raw materials and energy are used to make the goods
- *life* – chemicals and energy are needed to maintain and use the goods
- *death* – energy, and possibly space, is needed to recycle the goods or dispose of them as waste.

Here are some issues and questions that are being raised about the life cycle of polymers from the extraction of crude oil, through the production and use of commercial polymer products, to their eventual disposal.

Only about 4% of crude oil is used to make polymers. Most crude oil is used to provide fuel for transport, heating homes and industry. Although 'fracking' may provide further resources, if crude oil continues to be used at the present rate, known reserves are unlikely to last much into the next century.

1 Suggest three significant steps that should be taken to reduce the consumption of crude oil.

Large amounts of non-renewable fossil fuels are used in extracting crude oil, in transporting it to refineries, in processing at the refineries and then in the production of specific products such as plastic bags, bottles, toys and fibres.

After production, various polymer products are moved to shops where they are sold, used and then thrown away in landfill sites. This is very wasteful.

2 What are local councils and the government now doing to reduce landfill waste?

3 Why is this approach so important?

Most plastic waste can be melted and then remoulded. Recycling would seem an obvious way forward, but there are problems in sorting and separating different types of polymer, particularly when some products include more than one type of polymer. Polymers are classified into seven types for recycling purposes (see Table 6.2.1). The symbol of each type is clearly visible on plastic objects.

Sorting plastic waste into these different types is both difficult and costly, and until recently has been done by hand. Automatic methods have now been developed which use optical techniques, such as the use of infrared cameras. These are set to detect specific readings that are unique for each material. Other materials are then ejected from the conveyor belt using a jet of air.

4 Suggest any difficulties that an optical detector might have with a supply of household plastic waste.

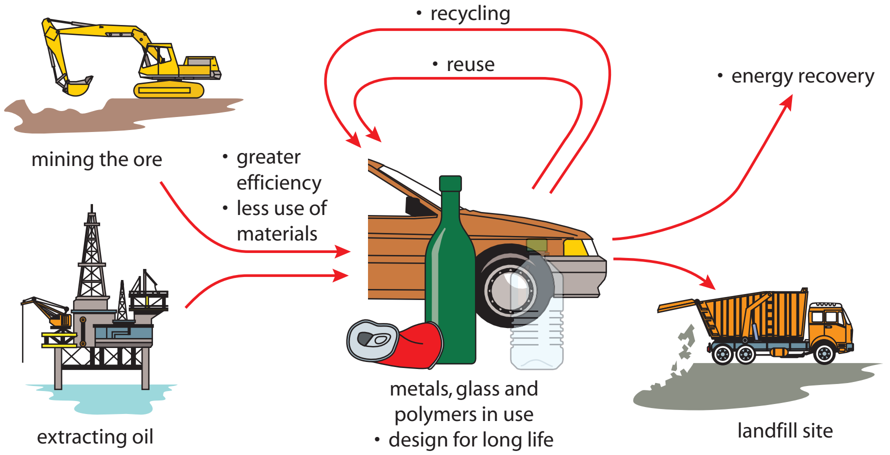


Figure 6.2.39 Processes and products can be redesigned to slow down the rate at which valuable resources are transformed into waste.

OPEN HERE
THIS BAG IS CERTIFIED COMPOSTABLE
BioBag

Figure 6.2.40 A plastic bag that is compostable.

Table 6.2.1 Types of plastic for recycling.

Polymer types	Examples of applications	Symbol
PETE or PET polyethylene terephthalate	Bottles for water and fizzy drinks	1 PET
HDPE high density polyethylene	Bottles for milk, juices, detergents	2 HDPE
PVC polyvinyl chloride	Clingfilm, pipes, window and door frames	3 PVC
LDPE low density polyethylene	Carrier bags, bin liners and packaging films	4 LDPE
PP polypropylene	Margarine tubs, microwaveable meal trays	5 PP
PS polystyrene	In expanded form, used as packaging and insulation	6 PS
Other	Types that do not fall into any of the above categories – or mixtures of polymers	7 OTHER

In some cases, it is possible to decompose the polymers to provide a feedstock for cracking. The polymers are shredded and heated in the absence of air in a process called pyrolysis. The vapours produced are cracked and the products distilled to produce liquid fuel, including diesel and kerosene.

5 **a)** Suggest where the energy comes from for the pyrolysis of polymers at high temperature.
b) Why are polyethylene or polypropylene used for pyrolysis but PVC is not?

Some polymers that are difficult to recycle can be burned and used as fuel. Incineration reduces the volume of the waste by a huge amount, but care is needed as toxic gases may be produced. Modern incinerators use very high temperatures to ensure the breakdown of any such gases into harmless products. Also, before the flue gases are released into the atmosphere they are cleaned to remove any pollutants.

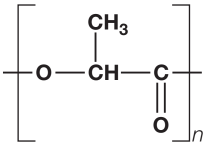
6 **a)** Is incineration better than landfill? Explain your answer.
b) Why are people often opposed to incinerators in their area?
c) What environmental problems does incineration make worse?
d) Gases including SO_2, NO_x and HCl are produced in an incinerator. How do chemists ensure that they are removed from the waste gases and do not enter the atmosphere?

When plastic bags were first produced and started to replace paper bags in the 1950s, they were hailed as a great success. Chemists had developed a new material that would not disintegrate when it got wet as a paper bags did. However the invention was just too good and its lack of any weakness has led to the problem of plastic waste today.

So chemists have now developed different materials to solve the waste problem. One solution has been to incorporate weak links in the addition polymer chain. Condensation polymers, such as starch or cellulose, contain polar functional groups which can be attacked by nucleophiles such as water. You will study condensation polymers in the second year of the A Level course. This hydrolysis breaks the polymer chain, so incorporating a few per cent of starch weakens the polymer and allows degradation into dust.

Perhaps a better solution is to produce bags (Figure 6.2.40) made entirely from condensation polymers such as PLA (polylactic acid) (Figure 6.2.41). These bags are completely biodegradeable and when used to wrap waste material will compost in months, rather than tens of years for traditional polythene bags. However, as with biofuels, growing the raw material for them competes with food production.

7 Why do you think that traditional polythene bags are still used? What is likely to bring an end to their use?



$$\left[-O-\overset{CH_3}{\overset{|}{CH}}-\underset{\underset{O}{\|}}{C}- \right]_n$$

Figure 6.2.41 The repeat unit of PLA, which despite its common name is actually a polyester made from lactic acid.

Key term

Addition polymerisation is an addition reaction in which small molecules, called monomers, join together forming a giant molecule, called a polymer.

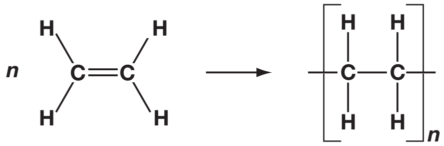


Figure 6.2.42 An overall equation for the polymerisation of ethene.

Tip

The abbreviation PVC comes from the original name for the polymer, which was polyvinyl chloride.

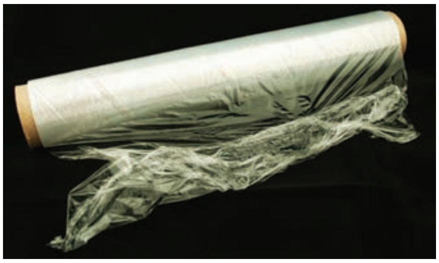


Figure 6.2.43 Clingfilm is usually made from PVC although alternatives such as LDPE are sometimes used.

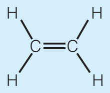
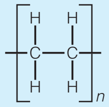
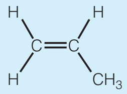
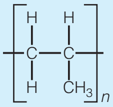
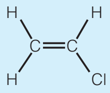
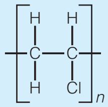
High-density polythene (HDPE) is manufactured at relatively low pressure and low temperature with a special catalyst. This produces extra long chains with very little branching, so the chains pack closer.

Processes like these are called 'addition polymerisations'. During **addition polymerisation**, small molecules like ethene, known as monomers, add to each other to form a giant molecule called a polymer. Addition polymers may contain several thousands of monomer units. A polymer can be represented by a repeat unit (Table 6.2.2). These units ignore the RO− group present on each end of a chain as they make up a negligibly tiny proportion of the whole polymer molecule. An overall equation for the polymerisation of ethene is shown in Figure 6.2.42.

Polythene is the most important addition polymer. Two other useful polymers are poly(propene) and poly(chloroethene) or PVC. These are also manufactured by addition polymerisation. Polythene, polypropene and PVC are soft, flexible and slightly elastic – because of this, they are often called plastics. One of their major advantages, apart from relatively low cost, is that they are almost chemically inert. This lack of reactivity, as well as being a benefit, can also be a problem where disposal of these plastics is concerned (see Activity: A more sustainable future for polymers). Some concern has been also expressed about the use of PVC to wrap food (Figure 6.2.43) because of the transfer to the food of compounds called plasticisers used in the film.

The monomers, polymer structures, properties and uses of polythene, polypropene and PVC are shown in Table 6.2.2.

Table 6.2.2 Some important addition polymers.

Monomer	Polymer repeat unit	Properties	Uses
Ethene 	Polythene (poly(ethene)) 	Light, flexible Easily moulded Transparent Good insulator Resistant to water, acids and alkalis	Plastic bags and bottles Beakers Insulation for cables Joint replacements
Propene 	Polypropene (poly(propene)) 	Tough Easily moulded Easily coloured Very resistant to water, acids and alkalis	Fibre for ropes and carpets Crates Toys
Chloroethene 	PVC (poly(chloroethene)) 	Tough Rigid or flexible Very resistant to water, acids and alkalis	Guttering and window frames Insulation for cables Waterproof clothing Flooring Clingfilm

Test yourself

30 $CF_2{=}CF_2$ is the monomer for the polymer PTFE.

a) What is the systematic name for $CF_2{=}CF_2$?

b) Draw a section of the PTFE polymer composed of three monomer units.

c) The name 'PTFE' contains four key letters from the full name of the polymer. What is the full name?

d) State one use for PTFE and the property of the polymer on which this use depends.

31 a) What conditions are used to manufacture low-density polythene?

b) Why is polythene so useful?

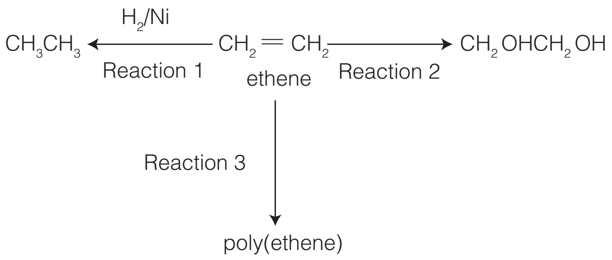
c) What is the major disadvantage of such plastics?

32 a) Why is only a small amount of initiator needed to make polymer chains of several thousand units long and why should the initiator not be described as a catalyst?

b) Using displayed formulae, write an equation for the polymerisation of propene.

Exam practice questions

1 The diagram shows three important reactions of ethene.



a) i) What conditions of temperature and pressure are used in Reaction 1? *(2)*

ii) Reaction 1 is used to convert unsaturated alkenes to saturated alkanes. What is meant by the terms 'unsaturated' and 'saturated' in this context? *(3)*

iii) Why are saturated and unsaturated chemicals important to dieticians? *(3)*

b) i) What chemicals are used in Reaction 2 to produce CH_2OHCH_2OH? *(2)*

ii) A common name for CH_2OHCH_2OH is ethylene glycol. What is its systematic name? *(1)*

iii) What is the common use of CH_2OHCH_2OH? *(1)*

c) i) What conditions are used in Reaction 3 to convert ethene to high-density poly(ethene)? *(2)*

ii) Draw a section of the poly(ethene) structure consisting of three monomer units. *(1)*

d) State four properties of poly(ethene) which make it particularly suitable for making plastic bags. *(2)*

2 Crude oil is an important source of materials for the petrochemical industry. Various products are obtained from crude oil by fractional distillation, followed by processes involving cracking and reforming.

a) How is crude oil separated into different fractions by fractional distillation? *(6)*

b) i) What is meant by 'cracking'? *(3)*

ii) Dodecane, $C_{12}H_{26}$, can be cracked into ethene and a straight-chain alkane so that the molar ratio of ethene to straight-chain alkane is 2:1.
Write an equation for this reaction and name the straight-chain alkane. *(2)*

iii) Heat alone can be used to crack alkanes, but oil companies normally use catalysts as well. Suggest two reasons why oil companies use catalysts. *(2)*

c) Straight-chain alkanes such as heptane can be reformed into cyclic compounds. Write an equation to show how heptane can be reformed into methylcyclohexane. *(2)*

d) Oxygen-containing compounds are added to some brands of petrol to improve their performance. In Formula One racing cars, 2-methylpropan-2-ol is usually added to the petrol.

i) Draw the structural formula of 2-methylpropan-2-ol. *(1)*

ii) Why do compounds like 2-methylpropan-2-ol improve a racing car's performance on the track? *(1)*

3 a) Write equations using molecular formulae for:

i) the complete combustion of pentane *(1)*

ii) the incomplete combustion of hexane to form a gaseous product *(1)*

iii) the incomplete combustion of heptane to form a solid product. *(1)*

b) State and explain a difference you would see in the flames of pentane and of pentene burning under identical conditions. *(2)*

4 a) The reaction between propene, $CH_3CH{=}CH_2$, and hydrogen bromide involves electrophilic addition and gives $CH_3CHBrCH_3$ as the major product.

i) Explain the term 'electrophilic addition'. *(3)*

ii) Give the name of the compound $CH_3CHBrCH_3$. *(1)*

iii) Draw displayed structures to show the mechanism of the reaction between propene and hydrogen bromide. *(4)*

iv) Explain why $CH_3CHBrCH_3$ is the major product rather than $CH_3CH_2CH_2Br$. *(3)*

b) Name the major product formed when propene reacts with iodine(I) chloride (ICl) and explain your answer. *(3)*

c) Write an equation for the reaction of propene with bromine water to form the major product. *(1)*

5 Heptane can undergo isomerisation to produce branched-chain alkanes such as 2-methylhexane and 2,3-dimethylpentane.

a) What is meant by the term 'isomerisation'? *(1)*

b) Write an equation using structural formulae for the isomerisation of heptane to 2-methylhexane. *(1)*

c) Write an equation using skeletal formulae for the isomerisation of heptane to 2,3-dimethylpentane. *(1)*

d) Draw and name the structure of one isomer of heptane with a name ending in butane. *(2)*

e) The boiling temperature of hexane is 69 °C and that of heptane is 99 °C. Why is the boiling temperature of heptane higher than that of hexane? *(2)*

f) The boiling temperature of 2,3-dimethylpentane is 84 °C. Predict the boiling temperature of 2-methylhexane and explain your prediction. *(2)*

6 Two isomeric hydrocarbons contain 85.7% carbon by mass and have $M_r = 84.0$

Isomer **X** decolorises an acidified solution of potassium manganate(VII) but isomer **Y** has no effect.

When isomer **Y** reacts with chlorine in the presence of UV light, only one monochloro-substituted product is formed.

There is also only one monochloro-substituted isomer of **X**, but this is not formed by reaction of **X** with chlorine.

a) Deduce the molecular formula of isomers **X** and **Y**. *(4)*

b) Draw the structure of **X** and of **Y** and of their monochloro-substituted compounds. *(4)*

c) Draw and name the compound formed when **X** reacts with chlorine. *(2)*

7 Propene and but-2-ene are used in the petrochemical industry to produce important polymers.

a) i) Explain the term 'polymer'. *(3)*

ii) Poly(propene) does not have a sharp melting temperature, but softens over a wide temperature range. Why is this? *(2)*

iii) Draw a section of the polymer formed from but-2-ene showing two repeat units. *(1)*

iv) Give two ways in which chemists contribute to a more sustainable use of materials such as poly(propene). *(2)*

b) But-2-ene can be converted to buta-1,3-diene by a process called dehydrogenation. Buta-1, 3-diene is used to make synthetic rubber.

i) Explain the term 'dehydrogenation'. *(1)*

ii) Draw the structure of buta-1,3-diene. *(1)*

iii) Write an equation for the dehydrogenation of but-2-ene to form buta-1,3-diene. *(2)*

8 A student studied the amount of unsaturation in a sample of vegetable oil by reacting samples of the oil with bromine water using the following practical instructions.

- Using a measuring cylinder, add 1 cm^3 of vegetable oil to a conical flask. Add 20 cm^3 of inert organic solvent to the flask.
- Fill a burette with bromine water and take the burette reading.
- Add the bromine water slowly from the burette to the solution in the conical flask. Shake the flask vigorously until the bromine colour disappears.
- Add more bromine water, shaking the flask after each addition, until the bromine water is no longer decolorised.
- Record the burette reading.
- Repeat the experiment.

The student obtained the following results.

Experiment	1	2	3
Volume of bromine water used/cm^3	8.3	7.8	9.0

a) Why was it necessary to shake the flask after each addition of bromine water? *(2)*

b) Describe what the student saw in the conical flask at the point where the bromine water was not decolorised. *(2)*

c) The student's results were not concordant. Suggest improvements to the experimental method which could give more concordant titres. *(3)*

d) The volumes of bromine water used were relatively small. Suggest improvements to the experimental method which would give larger titres. *(2)*

9 Ethane reacts with bromine in the gas phase to form bromoethane and hydrogen bromide.

$$C_2H_6(g) + Br_2(g) \rightarrow C_2H_5Br(g) + HBr(g)$$

Bond	**Bond enthalpy/kJ mol⁻¹**
C—H	412
C—C	348
C—Br	276
H—Br	366
Br—Br	193

a) Use the bond enthalpy data above to calculate the enthalpy change for this reaction. *(5)*

b) The mechanism of the reaction occurs in a series of steps. Write equations for the two steps which, when added together, give the overall equation above. Name this type of step. *(3)*

10 Chlorine reacts with an excess of propane in the presence of UV light to form a mixture of two isomers of chloropropane and very little dichloropropane.

a) Draw displayed structures of the two chloropropane isomers. *(2)*

b) Explain why little dichloropropane is formed under these conditions *(2)*

c) At low temperatures, the proportion of each chloropropane formed depends on the relative stabilities of the alkyl radicals formed during the reaction. The relative stabilities of radicals are similar to the relative stabilities of the equivalent carbocations. Suggest with explanation the proportion of each chloropropane formed at low temperatures. *(2)*

d) At higher temperatures, the proportion of each chloropropane in the product mixture is found to be as expected statistically. State this proportion. Explain your answer, stating any assumptions you have made. *(2)*

e) Why are the relative stabilities of intermediates less important as the temperature rises? *(1)*

11 A family of three drive their car about 8000 miles each year using 1000 dm^3 of petrol. Assuming that petrol consists of octane, C_8H_{18}, with a density of 0.8 $g\,cm^{-3}$, calculate the mass of carbon dioxide that their travel adds to the atmosphere in one year. *(6)*

6.3 Halogenoalkanes and alcohols

6.3.1 Halogenoalkanes

Halogenoalkanes are important to organic chemists both in research and in industry. Many halogenoalkanes are reactive compounds which can be converted into other more valuable products (Figure 6.3.1). This makes them useful as intermediates in synthesis – the production of one compound from another.

Figure 6.3.1 The Gore-tex® membrane in this waterproof jacket contains the fluoro compound poly(tetrafluorethene), $-(CF_2-CF_2)_n-$.

In the structure of a halogenoalkane, one or more of the hydrogen atoms in an alkane molecule is replaced by a halogen atom, for example:

CH_3F	fluoromethane
CH_3CH_2Cl	chloroethane
$CH_3CH_2CH_2Br$	1-bromopropane
$CH_3CH_2CH_2CH_2I$	1-iodobutane

The bond between carbon and the electronegative halogen atom is polar. This polarity affects the physical properties of halogenoalkanes (Section 6.3.2) and also their chemical properties (Section 6.3.4).

IUPAC rules name halogenoalkanes by placing the prefix fluoro, chloro, bromo or iodo before the name of the parent alkane.

Where necessary, the position of the halogen group is noted by including the number of the carbon to which it is attached – numbering either from left or right to give the lower number, for example, 1-iodobutane not 4-iodobutane.

If more than one halogen atom is present then the position of both must be given. If different types of halogen are present, as in CFCs (Section 6.3.5), the halogens are listed in alphabetical order.

CH_3CCl_3	1,1,1-trichloroethane
$BrCH_2CH_2Br$	1,2-dibromoethane
$CBrClF_2$	bromochlorodifluoromethane

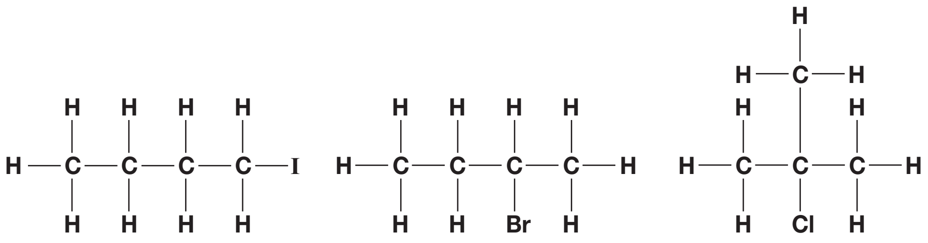
The terms **primary**, **secondary** and **tertiary** are used with halogenoalkanes and other organic compounds to show the positions of functional groups (Figure 6.3.2).

Key term

A **primary** halogenoalkane has the halogen atom bonded to a carbon at the end of the chain. A **secondary** halogenoalkane has the halogen atom bonded to a carbon in the middle of the chain but not at a branch. A **tertiary** halogenoalkane has the halogen atom bonded to a carbon at a branch in the chain.

Tip

The terms 'primary', 'secondary' and 'tertiary' have a different meaning when applied to amines which are derived from the ammonia molecule with one (primary), two (secondary) or three (tertiary) hydrogen atoms replaced by alkyl or aryl groups.



1-iodobutane (primary)

2-bromobutane (secondary)

2-chloro-2-methylpropane (tertiary)

Figure 6.3.2 Names and displayed formulae of three halogenoalkanes.

6.3.2 Physical properties of halogenoalkanes

Chloromethane, bromomethane and chloroethane are gases at room temperature, but most other halogenoalkanes are colourless liquids.

Their boiling points are higher than the parent alkane, because the polarity of the carbon–halogen bond leads to stronger intermolecular forces.

However, these dipole–dipole forces are much weaker than the hydrogen bonding that alcohols can form with water so, unlike alcohols, even small halogenoalkanes do not mix with water.

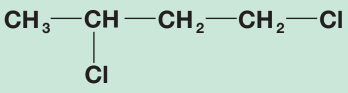
Test yourself

1 Draw the structures of the following compounds, and identify them as primary, secondary or tertiary:

- **a)** 1-iodopropane
- **b)** 2-chloro-2-methylbutane
- **c)** 3-bromopentane
- **d)** 1-bromo-2-chloropropane.

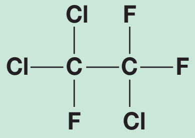
2 Name the following compounds.

a)

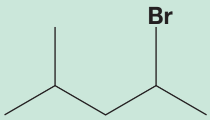


$CH_3—\underset{\displaystyle Cl}{\underset{|}{CH}}—CH_2—CH_2—Cl$

b)



c)



3 Which of the following molecules are polar and which are non-polar: $CHCl_3$, CH_2Cl_2, $CHCl_3$ and CCl_4?

4 The boiling temperatures of 1-chlorobutane, 1-bromobutane and 1-iodobutane are 352 K, 375 K and 404 K respectively. Suggest an explanation for the trend in values.

5 The boiling temperatures of the isomers 1-bromobutane, 2-bromobutane and 2-bromo-2-methylpropane are 375 K, 364 K and 346 K respectively. Suggest an explanation for the differences in boiling temperatures of the primary, secondary and tertiary compounds.

6 Explain why, despite containing a polar carbon–halogen bond, halogenoalkanes are immiscible with water.

6.3.3 The preparation of halogenoalkanes

Three types of reaction can be used to produce organic molecules containing halogen atoms.

From alkanes

Reaction of alkanes with chlorine or bromine, either on heating or on exposure to ultraviolet light, leads to free-radical substitution in which halogen atoms replace hydrogen atoms (Section 6.2.3).

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

From alkenes

Reaction of alkenes with hydrogen halides at room temperature produces halogenoalkane molecules containing one halogen atom (Section 6.2.9).

$$CH_3CH{=}CHCH_3(g) + HBr \rightarrow CH_3CH_2CHBrCH_3$$

Alkenes also react with halogen elements to form halogenoalkane molecules containing two halogen atoms.

$$CH_3CH{=}CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$$

From alcohols

Alcohols react with phosphorus halides or hydrogen halides to form halogenoalkanes.

$$C_2H_5OH(l) + PCl_5(s) \rightarrow C_2H_5Cl(l) + POCl_3(l) + HCl(g)$$

$$CH_3CH_2CH_2OH(l) + HCl(aq) \rightarrow CH_3CH_2CH_2Cl(l) + H_2O(l)$$

On a laboratory scale, the usual preparative methods are based on the reactions of alcohols with a hydrogen halide, or with a phosphorus halide (Section 6.3.8).

Test yourself

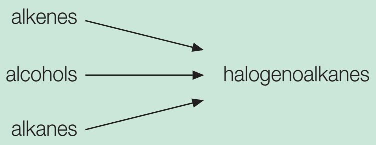
7 Name the five halogenoalkanes produced in the reactions in Section 6.3.3.

8 a) Write an equation to show the formation of 1-bromobutane from butane. Give a necessary condition for the reaction and explain why 1-bromobutane is not the only organic product.

b) Write an equation for a possible preparation of 1-bromobutane from but-1-ene. Explain why a low yield of 1-bromobutane is obtained in this reaction.

c) Write an equation for a preparation of 1-bromobutane that is more efficient than those in parts (a) and (b).

9 Give the reagents and name the three types of reaction used to make halogenoalkanes as shown in the scheme below.



6.3.4 Chemical reactions of halogenoalkanes

The polarity of the carbon–halogen bond means that the carbon atom in the bond is slightly electron deficient. This δ+ atom is, therefore, vulnerable to attack by **nucleophiles**. The two important reactions of halogenoalkanes are **substitution** and **elimination** (Section 6.1.6).

Substitution by reaction with water

Cold water slowly hydrolyses halogenoalkanes, replacing the halogen atoms with an –OH group to form alcohols.

$$CH_3CH_2CH_2I(l) + H_2O(l) \rightarrow CH_3CH_2CH_2OH(l) + H^+(aq) + I^-(aq)$$

The nucleophile in this nucleophilic substitution reaction is the water molecule. The rate of **hydrolysis** of different halogenoalkanes can be compared by carrying out the reaction in the presence of silver ions. The halogen atoms in halogenoalkanes are covalently bonded to carbon. They cannot react with silver ions and so give no precipitate of a silver halide. Hydrolysis releases halide ions, which immediately react with silver ions to form precipitates of silver halides (Section 4.10).

Halogenoalkanes do not mix with water or aqueous solutions. For this reason, the reaction is carried out in the presence of ethanol, which can dissolve the halogenoalkane and also mix with the aqueous silver nitrate.

Key terms

Nucleophiles are electron pair donors (Section 6.1.7).

Substitution is a reaction in which one atom or group is replaced by another atom or group.

Elimination is a reaction which produces an unsaturated product by loss of atoms or groups from adjacent carbon atoms.

Hydrolysis is a reaction in which a compound splits apart in a reaction involving water.

Core practical 4

Investigation of the rates of hydrolysis of halogenoalkanes

A student studied the hydrolysis of 1-chlorobutane, 1-bromobutane and 1-iodobutane to investigate the effect of the halogen atom on the rate of hydrolysis. A similar method was also used to compare the rates of hydrolysis of three isomeric bromoalkanes: one primary, one secondary and one tertiary.

The student followed the instructions labelled **A** to **D**. The results are shown below the method on page 206.

The effect of the halogen atom on the rate of hydrolysis

A Set up three labelled test tubes as shown in the table. Stand the tubes in a water bath at about 60 °C. Put a tube containing 5 cm^3 silver nitrate solution in the same beaker. Leave the tubes for about 10 minutes to allow them to reach the temperature of the water bath.

Tube 1	Tube 2	Tube 3
1 cm^3 ethanol	1 cm^3 ethanol	1 cm^3 ethanol
2 drops 1-chlorobutane	2 drops 1-bromobutane	2 drops 1-iodobutane

B Note the time. Quickly add 1 cm^3 of the warm silver nitrate solution to each of the three tubes. Shake the tubes to mix the contents. Replace them in the water bath and observe for the next five minutes or so.

Results

Tube 1	Tube 2	Tube 3
No precipitate after 5 minutes.	Cream precipitate appears between 2 and 3 minutes.	A heavy yellow precipitate is visible after 1 minute.

1 What was the purpose of adding ethanol to the tubes?
2 In what ways did the experiment try to ensure that the only factor that affected the rate of reaction was the halogen atom?
3 Suggest any improvements to the method to make the comparison fairer.
4 Identify the precipitates and explain why they formed slowly and not immediately.
5 Which halogenoalkane hydrolysed fastest and which slowest?
6 What is the order of polarity of the carbon–halogen bonds? What are the bond energies of the three carbon–halogen bonds? Does the rate of hydrolysis correlate better with bond polarity or bond strength?

The effect of the structure of the carbon skeleton on the rate of hydrolysis

C Set up three labelled test tubes as shown in the table. This time there is no need to warm the tubes.

Tube 1	Tube 2	Tube 3
1 cm^3 ethanol	1 cm^3 ethanol	1 cm^3 ethanol
2 drops 1-bromobutane	2 drops 2-bromobutane	2 drops 2-bromo-2-methylpropane

D Note the time. Quickly add 1 cm^3 of silver nitrate solution to each of the three tubes. Observe the tubes for the next five minutes or so.

Results

Tube 1	Tube 2	Tube 3
Cream precipitate appears between 2 and 3 minutes.	Cream precipitate appears between 1 and 2 minutes.	Cream precipitate appears in under a minute.

7 Suggest any improvements to the method to make the comparison as fair as possible.
8 What might account for the differing rates of hydrolysis of the three compounds?

Substitution by reaction with hydroxide ions

Replacement of the halogen atom of a halogenoalkane by an –OH group is much quicker with an aqueous solution of an alkali, such as potassium or sodium hydroxide (Figure 6.3.3). Heating increases the rate of reaction even further.

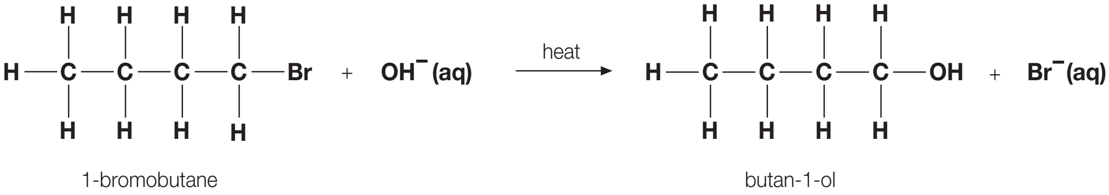


Figure 6.3.3 Reaction of a halogenoalkane with an alkali on heating.

The nucleophile in this nucleophilic substitution reaction is the hydroxide ion. The bromide ion released into the solution will react with silver ions to form a cream precipitate of silver bromide.

The red curly arrows in the mechanism (Figure 6.3.4) show the movement of electron pairs.

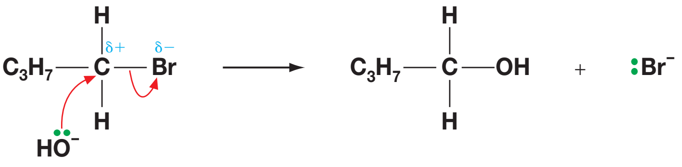

H
δ+
δ−
C_3H_7—C—Br
H
HO^-
H
C_3H_7—C—OH
H
+
:Br^-

Figure 6.3.4 A nucleophilic substitution mechanism using hydroxide ions.

Tip

Take care when using C_3H_7– in structures as it does not show whether the alkyl group attached is $CH_3CH_2CH_2$– or $(CH_3)_2CH$–.

Hydrolysing halogenoalkanes makes it possible to distinguish between chloro-, bromo- and iodo- compounds (Figure 6.3.5).

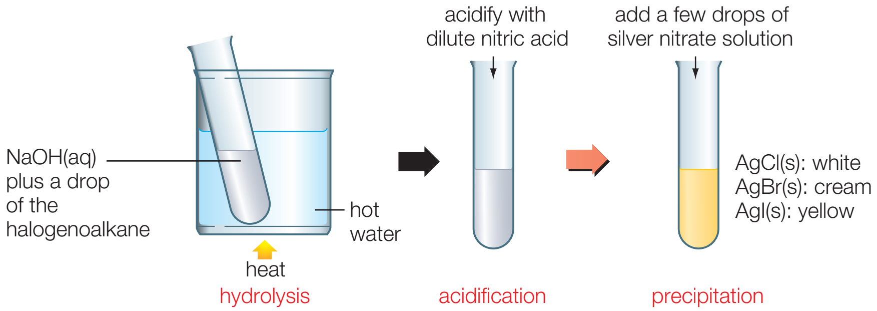

NaOH(aq) plus a drop of the halogenoalkane
hot water
heat
hydrolysis
acidify with dilute nitric acid
acidification
add a few drops of silver nitrate solution
AgCl(s): white
AgBr(s): cream
AgI(s): yellow
precipitation

Figure 6.3.5 Heating the compound with an alkali releases halide ions. Acidifying with nitric acid and then adding silver nitrate produces a precipitate of the silver halide.

Test yourself

10 Explain the use of the terms ‘nucleophile’, ‘substitution’ and ‘hydrolysis’ to describe the reaction of halogenoalkanes with water.

11 Write equations for the two reactions which take place when 2-bromobutane reacts with water in the presence of silver ions, Ag^+.

12 Refer to Figure 6.3.5 in answering this question.

- **a)** Why is hydrolysis necessary before testing with silver nitrate?
- **b)** Why must nitric acid be added before the silver nitrate solution?
- **c)** Write the equations for the three reactions that take place when detecting bromide ions in 1-bromobutane by this method.

13 Suggest why the polymer, PTFE, $-(CF_2-CF_2)_n-$ is unaffected by prolonged exposure to boiling water or hot alkali.

Key terms

Heating **under reflux** means heating with a condenser placed vertically in the flask.

A **reflux condenser** is fitted vertically in a flask to prevent vapour escaping while a liquid is being heated. Vapour from the boiling reaction mixture condenses and flows back into the flask.

Substitution by reaction with cyanide ions

When a halogenoalkane is heated **under reflux** with a solution of potassium cyanide in ethanol, the halogen atom is replaced by the CN group and a compound called a nitrile is formed. Use of a **reflux condenser** (Figure 6.3.6) ensures that the volatile substances, the halogenoalkane and ethanol, condense and drip back into the reaction mixture. This nucleophilic substitution

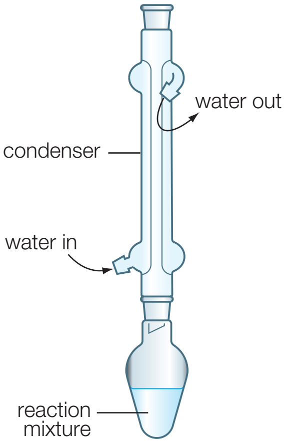

water out
condenser
water in
reaction mixture

Figure 6.3.6 Apparatus for heating under reflux.

reaction, where the cyanide ion acts as a nucleophile, is useful in synthesis as a way of increasing the length of the carbon chain in a molecule (Figure 6.3.7).

For example, the two-carbon chain in bromoethane becomes three in propanenitrile.

$$\underset{\text{bromoethane}}{CH_3CH_2Br} + CN^- \rightarrow \underset{\text{propanenitrile}}{CH_3CH_2CN} + Br^-$$

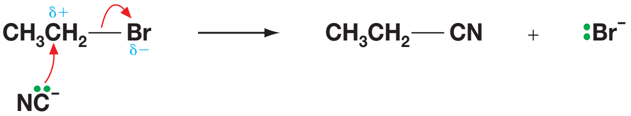


Figure 6.3.7 A nucleophilic substitution mechanism using cyanide ions.

Substitution by reaction with ammonia

Warming a halogenoalkane with a concentrated solution of ammonia in ethanol in a sealed tube produces a primary amine.

The ammonia molecule acts as the nucleophile. In the presence of excess ammonia, the other product is an ammonium salt (Figure 6.3.8).

The mechanism for this reaction, a nucleophilic substitution, occurs in two steps (Figure 6.3.9).

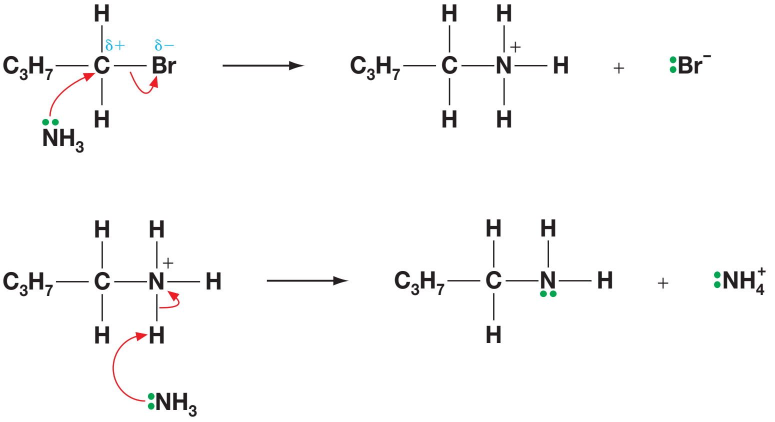


Figure 6.3.9 A nucleophilic substitution mechanism using ammonia.

The reactivity of ammonia as a nucleophile depends on the lone pair of electrons on its nitrogen atom. A problem in this case is that there is also a lone pair on the nitrogen atom of the primary amine formed and this is even more reactive because of the inductive effect of the alkyl group. So the primary amine can also react with the halogenoalkane and this can lead to a mixture of further products. Fortunately, it is possible to limit further reaction by using an excess of ammonia, so that there is a much greater chance of ammonia – rather than the amine – acting as nucleophile with the halogenoalkane molecules.

Tip

It is necessary to state that an excess of ammonia is used in the formation of a primary amine from a halogenoalkane. For each reaction in organic chemistry, you should learn not only the reagents, but also the reaction conditions. The same reagents may give different products under different reaction conditions.

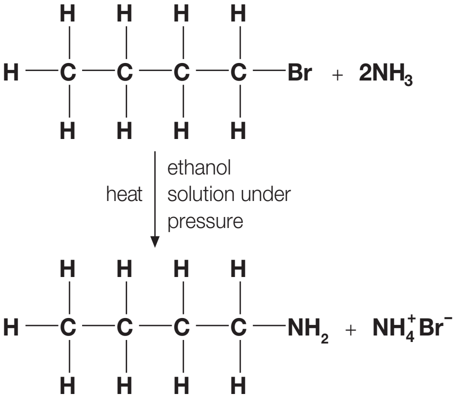


Figure 6.3.8 Reaction of 1-bromobutane with ammonia to make butylamine (1-aminobutane).

Tip

Hydrogenation of a C≡N bond in the presence of a nickel catalyst forms a primary amine. This reaction produces a pure product. The alternative preparation of amines by substitution in halogenoalkanes using ammonia can lead to an impure product because of the possibility of further substitution.

Test yourself

14 **a)** Write an equation for the formation of butanenitrile in a reaction using potassium cyanide.

b) Name the organic starting material and state the conditions needed.

c) Aqueous solutions of potassium cyanide are alkaline. Name another product in the reaction to form butanenitrile if aqueous conditions are used.

15 Refer to the mechanism for the reaction of ammonia with 1-bromobutane in answering this question.

a) Describe the behaviour of the ammonia molecule in the first step.

b) Describe the behaviour of the ammonia molecule in the second step.

16 Write an overall equation for the reaction of an excess of ammonia with bromoethane.

17 Suggest the structure of the organic product when ethylamine reacts with bromoethane. Can this product also react with bromoethane? If so, what is formed?

Elimination reactions

In the reaction of aqueous potassium hydroxide with a halogenoalkane (Figure 6.3.3), the hydroxide ion acts as a nucleophile and brings about substitution. But in an alternative reaction in ethanolic solution, the hydroxide ion acts as a base and brings about elimination of a hydrogen halide to form an alkene instead of substitution. The mechanism shown in Figure 6.3.10 is not required for your specification.

$$CH_3CHBrCH_3 + OH^- \rightarrow CH_3CH{=}CH_2 + H_2O + Br^-$$

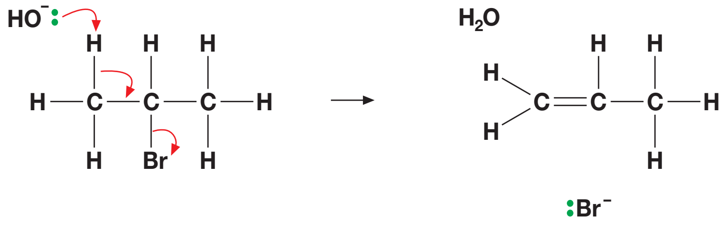


Figure 6.3.10 Elimination of hydrogen bromide from 2-bromopropane on heating with a solution of potassium hydroxide in ethanol.

The hydroxide ion provides both the electrons needed to form a new bond to the hydrogen atom. The C–H bond breaks and the pair of electrons from that bond forms a second bond between the two carbon atoms. At the same time, the C–Br bond breaks heterolytically. In this case, both electrons in the bond leave with the bromine atom, which is set free as a bromide ion.

Although changing the reaction conditions can favour substitution or elimination, the result of these reactions is usually a mixture of products (Figure 6.3.11). Also, elimination happens more readily with secondary or tertiary halogenoalkanes and substitution more readily with primary halogenoalkanes.

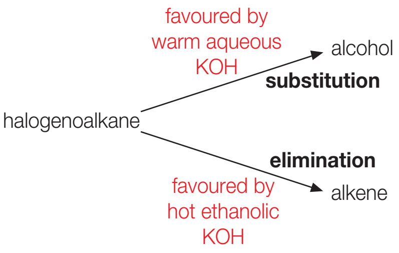


Figure 6.3.11 Alternative reactions of a halogenoalkane with solutions of hydroxide ions.

Activity

The preparation of 1-bromobutane from butan-1-ol

Figure 6.3.12 shows the steps in synthesising a pure sample of 1-bromobutane from butan-1-ol. The alcohol reacts with hydrogen bromide formed from sodium bromide and 50% sulfuric acid.

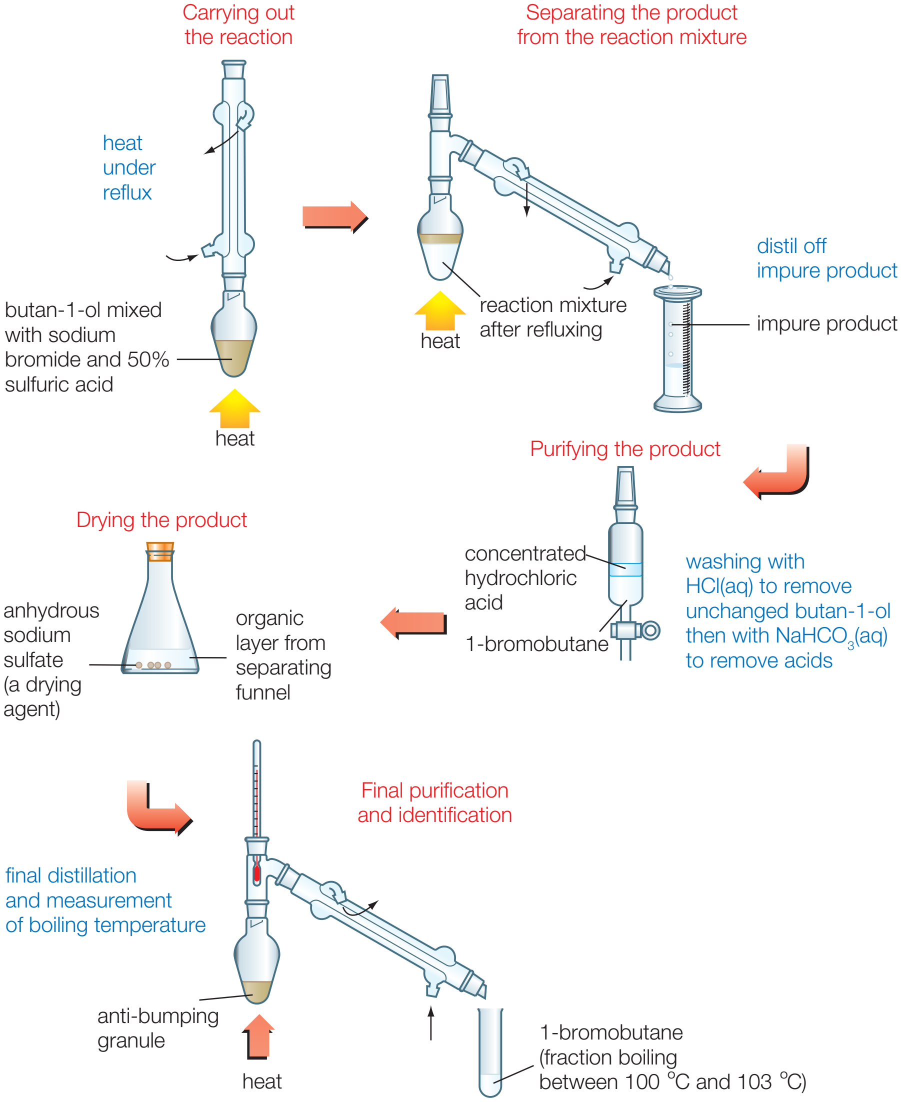

Carrying out the reaction
heat under reflux
butan-1-ol mixed with sodium bromide and 50% sulfuric acid
heat
Separating the product from the reaction mixture
distil off impure product
impure product
heat
reaction mixture after refluxing
Purifying the product
concentrated hydrochloric acid
1-bromobutane
washing with HCl(aq) to remove unchanged butan-1-ol then with NaHCO$_3$(aq) to remove acids
Drying the product
anhydrous sodium sulfate (a drying agent)
organic layer from separating funnel
Final purification and identification
final distillation and measurement of boiling temperature
anti-bumping granule
heat
1-bromobutane (fraction boiling between 100 °C and 103 °C)

Figure 6.3.12 Steps in the synthesis of 1-bromobutane from butan-1-ol.

1 **a)** Identify three aspects of this preparation that might be hazardous.
  b) What steps would you take to reduce the risks from these hazards?

2 Write an equation for the reaction of sodium bromide with 50% sulfuric acid to form hydrogen bromide.

3 Explain why 50% sulfuric acid is used, and not concentrated sulfuric acid.

4 The reaction mixture is heated for about 40 minutes but even after this time some of the alcohol does not turn into the product. Suggest a reason why.

5 Explain why the reaction flask is fitted with a reflux condenser.

6 After heating the reaction mixture for some time, the flask contains a mixture of chemicals including 1-bromobutane, unchanged butan-1-ol, hydrogen bromide and unchanged sodium bromide. Which of these chemicals is likely to distil over and collect in the measuring cylinder when separating the impure product?

7 Why are there two layers in the separating funnel when the product is shaken with aqueous reagents?

8 Suggest a reason why shaking the product with hydrochloric acid helps to remove unchanged butan-1-ol from the impure product.

9 Why is aqueous sodium hydrogencarbonate used in the separating funnel, and not aqueous sodium hydroxide, to remove acidic impurities?

10 Explain the term ‘fraction’ to describe the sample of product collected during the final distillation.

11 When this synthesis was carried out, the yield was 6.8 g of 1-bromobutane from 7.5 cm^3 butan-1-ol. The density of butan-1-ol is 0.81 g cm^{-3}. Calculate the percentage yield.

12 Suggest three reasons why the percentage yield is below 100%.

Tip

For the differences between hazards and risks, refer to Practical skills sheet 2, ‘Assessing hazards and risks’, which you can access via the QR code for Chapter 6.3 on page 313.

Test yourself

18 Give the name and structure of the main organic product when 2-bromopropane reacts on heating with:

  a) an aqueous solution of sodium hydroxide.

  b) a solution of potassium hydroxide in ethanol.

19 Outline mechanisms to show how both but-1-ene and but-2-ene can be formed when 2-bromobutane reacts with a hot solution of potassium hydroxide in ethanol.

20 Consider the mechanisms for the competing substitution and elimination reactions of haloalkanes with hydroxide ions and suggest why elimination is favoured at higher temperatures.

6.3.5 The uses of halogenoalkanes and their impacts

The discovery, production and use of halogenoalkanes during the last century have led to dramatic examples of the way in which science-based technology can provide us with products we value, and which make our lives more comfortable and safer. Yet, at the same time, these new technologies can turn out to have unintended and undesirable consequences.

One particular class of unreactive halogenoalkanes is notorious because of the damaging effect they have had on the Earth's ozone layer. These are called chlorofluorocarbons (CFCs) and were developed in the early twentieth century, supposedly as safe alternatives to toxic refrigerants such as ammonia and sulfur dioxide. As CFCs are also powerful greenhouse gases, their use is doubly damaging.

There are now increasing restrictions on the uses of halogenoalkanes because of concerns about their hazards to health, their persistence in the environment and their effect on the ozone layer (Figure 6.3.13).

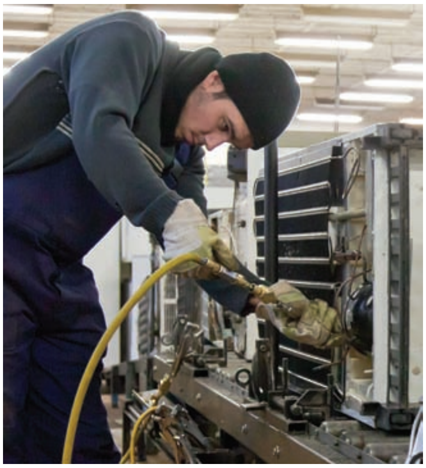


Figure 6.3.13 A recycling plant which recovers CFCs from the coolant systems of old refrigerators and freezers. The CFCs are removed from the systems as gases, liquefied and then chemically destroyed.

Halogenoalkanes are used as:

- solvents, for example CH_2Cl_2
- refrigerants, for example CF_3CH_2F, which has replaced the CFC CF_2Cl_2
- fire extinguishers and fire retardants, for example C_3HF_7, which has replaced halons such as CBr_2ClF.

Chlorofluorocarbons (CFCs) are compounds containing just the elements chlorine, fluorine and carbon, such as CCl_3F, CCl_2F_2 and CCl_2FCClF_2. They contain no hydrogen. CFCs have some desirable properties – they are unreactive, do not burn and are not toxic. It is also possible to make CFCs with different boiling temperatures to suit different applications. These properties made CFCs ideal as the working fluid in refrigerators and air-conditioning units. They can also act as the blowing agents to make the bubbles in expanded plastics and insulating foams. CFCs were once valued as good solvents for dry cleaning and for removing grease from electronic equipment.

The manufacture of CFCs and their general use was banned by the Montreal Protocol in 1987 because of their effects on the ozone layer.

CFCs can also contribute to global warming. In 1987, governments also agreed to ban the production of bromofluoroalkanes, which were then in common use as halon fire extinguishers in homes, on aircraft and on ships, as well as in a wide range of electronic equipment.

Since the Montreal Protocol, the concentration of CFCs in the atmosphere has been falling, after peaking in 1994. The Antarctic ozone 'hole' has begun to decrease but complete recovery of the ozone layer to pre-1980 levels is not predicted until 2060.

These bans set chemists the challenge of finding replacement chemicals with similar properties to CFCs, but without the harmful impacts on the environment. The chemists' first step was to try the effect of adding hydrogen to make hydrochlorofluorocarbons (HCFCs). These are much less stable in the lower atmosphere and were expected to break down before reaching the ozone layer. But these were still found to deplete the ozone layer and have been banned after 2020. More recently, new chemicals have been made that contain no chlorine. These are hydrofluorocarbons (HFCs), which survive for an even shorter time in the lower atmosphere. HFCs have no effect on the ozone layer, but they are greenhouse gases.

Bio Ethanol
85%

Figure 6.3.14 This fuel is a blend of conventional petrol and 85% bioethanol. Using a mixture of the two fuels produces less carbon in the vehicle exhaust emissions than using petrol alone.

Tip

The name of an alcohol ends in -ol. So if the name of any compound ends in -ol, for example, cholesterol or paracetamol, there must be an alcohol group present, even if the rest of the molecule is complicated.

6.3.6 Alcohol names and structures

Compounds which contain the –OH functional group are called alcohols. Ethanol is the best known member of this family because it is easily produced by fermentation and is the alcohol in beer, wine and spirits. Because it is so common, the person in the street will often say 'alcohol' when they mean ethanol. But to the chemist, there are many alcohols with different properties and uses. Alcohols are useful solvents in the home, in laboratories and in industry and so called 'bioethanol' is an important fuel (Figure 6.3.14). Understanding the properties of the –OH functional group in alcohols helps to make sense of the reactions of some important biological compounds, especially carbohydrates such as sugars and starch.

Alcohols are compounds with the formula R–OH, where R represents an alkyl group. The hydroxy group, –OH, is the functional group which gives alcohols their characteristic reactions.

The simplest alcohols are:

- methanol CH_3OH
- ethanol CH_3CH_2OH
- propan-1-ol $CH_3CH_2CH_2OH$.

IUPAC rules name alcohols by replacing the 'e' at the end of the corresponding alkane with '-ol' – so ethane becomes ethanol.

Where necessary, the position of the –OH group is noted by including the number of the carbon to which it is attached – numbering either from left or right to give the lower number, e.g. propan-1-ol not propan-3-ol.

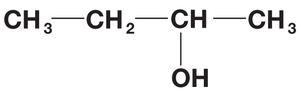
The terms **primary**, **secondary** and **tertiary** are used with alcohols and other organic compounds to show the positions of functional groups (Figure 6.3.15).

Key terms

A **primary** alcohol has the –OH group at the end of the chain. A **secondary** alcohol has the –OH group in the middle of the chain but not at a branch. A **tertiary** alcohol has the –OH group at a branch in the chain.

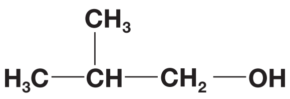
$\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH}$

butan-1-ol
a primary alcohol



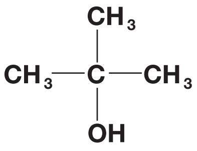
$$\mathrm{CH_3{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_3}$$

butan-2-ol
a secondary alcohol



$$\mathrm{H_3C{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_2{-}OH}$$

2-methylpropan-1-ol
a primary alcohol



$$\mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}{-}CH_3}$$

2-methylpropan-2-ol
a tertiary alcohol

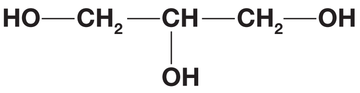
Figure 6.3.15 The names and structures of the four isomeric alcohols with the formula C_4H_9OH.

Tip

The final 'e' is not removed when naming an alcohol containing more than one –OH group. In these cases the ending diol or triol is added after the numbers which show the positions of the –OH groups, for example, ethane-1,2-diol and propane-1,2,3-triol below.

$\mathrm{HO{-}CH_2{-}CH_2{-}OH}$

ethane-1,2-diol



$$\mathrm{HO{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_2{-}OH}$$

propane-1,2,3-triol

Test yourself

21 Draw the structural formulae of these alcohols, and state whether they are primary, secondary or tertiary compounds:

a) propan-1-ol **b)** propan-2-ol

c) 2-methylbutan-2-ol **d)** 3-methylbutan-2-ol.

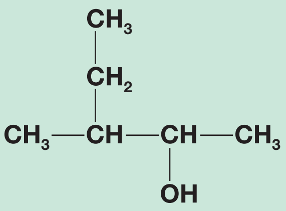
22 Draw the skeletal formula and name one isomer with the formula $C_5H_{11}OH$ that is:

a) a primary alcohol **b)** a secondary alcohol

c) a tertiary alcohol.

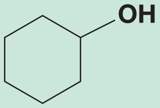
23 Name the following alcohols and classify each OH group as primary, secondary or tertiary:

a)

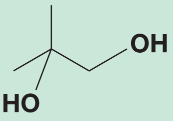


$$\mathrm{CH_3{-}\overset{\overset{\overset{\overset{CH_3}{|}}{CH_2}}{|}}{CH}{-}\underset{\underset{OH}{|}}{CH}{-}CH_3}$$

b)



c)



6.3.7 Physical properties of alcohols

Although methane and ethane are gases at room temperature, the simplest alcohols, methanol and ethanol, are liquids under the same conditions. Alcohols are much less volatile than hydrocarbons that have roughly the same molar mass. This is because the hydrogen bonding between –OH groups in alcohols is much stronger than the London forces between alkanes (Section 2.6). For the same reason, alcohols with short hydrocarbon chains also mix completely with water.

If two or three –OH groups are present, the intermolecular hydrogen bonding becomes even stronger. This can lead to very viscous liquids such as propane-1,2,3-triol (commonly known as glycerol) or solids such as glucose.

Test yourself

24 Refer to the data sheet for Chapter 6.3, 'Melting and boiling temperatures of some alkanes and alcohols', which you can access via the QR code for this chapter on page 313. Use data from this data sheet to show that alcohols are less volatile than alkanes with similar molar masses.

25 **a)** Draw a diagram to show the hydrogen bonding between a methanol molecule and a water molecule.

b) Explain why hydrogen bonding accounts for the fact that methanol, at room temperature, is a liquid that mixes freely with water, while ethane is a gas which is insoluble in water.

26 A half-full bottle of propan-1-ol is stoppered and shaken for a few seconds. When the shaking is stopped, the bubbles of air escape from the liquid very quickly. By contrast, after a half-full bottle of propane-1,2,3-triol is shaken in a similar way, the bubbles of air rise very slowly. Suggest why there is a difference in behaviour of the two liquids.

6.3.8 Chemical properties of alcohols

Alcohols are much more reactive than alkanes because the C–O and O–H bonds in the molecules are polar (see Section 2.5).

Combustion

Alcohols burn in a plentiful supply of air with a clean, pale blue flame. Methanol and ethanol are both common fuels (see Section 6.2.6) and fuel additives.

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

Tip

When balancing equations for the combustion of alcohols, don't forget the oxygen atom in the alcohol.

Tip

It is often convenient to write an equation for the combustion of one mole of alcohol and use fractions of moles of oxygen, for instance:

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Substitution of the –OH group by a halogen atom

The –OH group in an alcohol can be replaced by a halogen atom. This is an example of a substitution reaction. Several reagents can be used, including phosphorus halides or some hydrogen halides.

Chloroalkanes are best prepared from alcohols using phosphorus(v) chloride.

$$C_3H_7OH(l) + PCl_5(s) \rightarrow C_3H_7Cl(l) + POCl_3(l) + HCl(g)$$

Tertiary chloroalkanes can be prepared by reacting tertiary alcohols with concentrated hydrochloric acid. For instance, a tertiary chloroalkane can be made at room temperature by reacting the alcohol, 2-methylpropan-2-ol, with concentrated hydrochloric acid (see Core practical 6 on page 216). The reaction of concentrated hydrochloric acid with primary alcohols is very slow and not suitable for synthesis.

Bromoalkanes are conveniently prepared from alcohols using hydrogen bromide. For example, butan-1-ol reacts with hydrogen bromide on heating in the presence of sulfuric acid to form 1-bromobutane. It is usual to make the hydrogen bromide in the reaction flask by mixing 50% sulfuric acid with sodium or potassium bromide (see the Activity in Section 6.3.4, page 210).

$$C_4H_9OH(l) + HBr(aq) \rightarrow C_4H_9Br(l) + H_2O(l)$$

Bromoalkanes can also be made from alcohols using phosphorus(v) bromide or phosphorus(III) bromide.

$$3C_3H_7OH(l) + PBr_3(s) \rightarrow 3C_3H_7Br(l) + H_3PO_3(l)$$

Iodoalkanes can be made by reacting alcohols with phosphorus(III) iodide, but, as phosphorus(III) iodide is unstable, it is made in the reaction flask using a mixture of red phosphorus and iodine. Once formed, it reacts with the alcohol.

$$3C_3H_7OH(l) + PI_3(s) \rightarrow 3C_3H_7I(l) + H_3PO_3(l)$$

Hydrogen iodide is unstable with respect to its elements and also easily oxidised to iodine, so cannot be used to prepare iodoalkanes.

Tip

The reaction with phosphorus(v) chloride also produces hydrogen chloride gas, which is seen as misty fumes. This observation makes the reaction a useful test for the presence of the –OH group in molecules.

Tip

Beware that C_3H_7OH is an ambiguous formula as it represents both propan-1- ol and propan-2-ol and does not specify which. Both alcohols react in the same way with PCl_5, so this formula is suitable. However, propan-1-ol, $CH_3CH_2CH_2OH$, and propan-2-ol, $CH_3CH(OH)CH_3$, react in different ways with oxidising agents, so more precise structures should be used in those cases.

Test yourself

27 Write equations for:

- **a)** the complete combustion of propan-1-ol in a plentiful supply of air
- **b)** the incomplete combustion of butan-1-ol in a limited supply of air to form carbon and water.

28 Write an equation for the formation of 2-bromobutane from butan-2-ol and hydrogen bromide.

29 Describe a test to confirm that hydrogen chloride is formed when PCl_5 reacts with an alcohol.

30 Write an equation for the formation 1-iodobutane from butan-1-ol.

31 Why is it not possible to convert an alcohol into an iodoalkane using a mixture of potassium iodide and concentrated sulfuric acid?

Tip

Bromide ions are protonated by concentrated sulfuric acid to form HBr. But bromide ions are also oxidised by concentrated sulfuric acid, so the reaction mixture turns orange because of the formation of bromine (Section 4.10).

Core practical 6

Chlorination of 2-methylpropan-2-ol with concentrated hydrochloric acid

A sample of 2-chloro-2-methylpropane is prepared using the procedure outlined in steps **A–K**.

Preparation

A Add about 10 cm^3 of 2-methylpropan-2-ol to a measuring cylinder. Weigh the cylinder and contents.

B Pour the alcohol into a 250 cm^3 conical flask and reweigh the measuring cylinder. Add, a little at a time, a total of 35 cm^3 of concentrated hydrochloric acid. Stopper and swirl the flask to mix the contents.

C After adding all the acid, leave the stoppered flask to stand for about 20 minutes in a fume cupboard. Shake the mixture carefully from time to time releasing the pressure after each shaking. During this time, set up a clean distillation apparatus in a fume cupboard or in a well-ventilated laboratory.

Separation and purification

D Add about 3 g of powdered anhydrous calcium chloride to the flask. Shake to dissolve.

E Pour the contents of the flask into a tap funnel. Allow the two layers to separate. Run off the lower layer.

F Neutralise your product in the tap funnel by adding a solution of sodium hydrogencarbonate, 2 cm^3 at a time. Stopper and shake after each addition. Take care to release the pressure. Continue until no more carbon dioxide forms when you add alkali.

G Allow the layers to separate and run off the lower layer. Pour your product into a small, dry conical flask.

H Add 2–3 small spatula measures of anhydrous sodium sulfate to the flask. Swirl the mixture. Stopper and allow to stand for about 5 minutes.

I Carefully pour your product through a small funnel fitted with a plug of cotton wool into the pear-shaped distillation flask. Add a few anti-bumping granules. Weigh the receiving flask and reassemble the distillation apparatus (Figure 6.3.16).

J Distil the product. Heat gently. Continue heating just strongly enough to distil the liquid at a rate of not more than about 2 drops per second. Collect the fraction that boils between 48 °C and 52 °C.

K Reweigh the receiving flask to determine the yield.

Questions

1 Write an equation for the reaction showing the structure of both organic compounds.

2 What are the main hazards associated with use of 2-methylpropan-2-ol and concentrated hydrochloric acid, and what precautions should be taken? (Refer to Practical skills sheet 2, ‘Assessing hazards and risks’, which you can access via the QR code for Chapter 6.3 on page 313.)

3 Suggest a reason why the preparation can be carried out at room temperature.

4 List the steps taken to purify the product and identify the impurities removed at each stage.

5 Why is sodium hydrogencarbonate used in the purification process instead of a stronger alkali such as sodium hydroxide?

6 Describe how the pressure is released in Stage F.

7 Which layer contains the chloroalkane in Stage G?

8 What is the plug of cotton wool for in Stage I?

9 Why is the distillation an example of fractional distillation?

10 The density of 2-methylpropan-2-ol is 0.786 g cm^{-3}. In an experiment, 0.75 g of 2-chloro-2-methylpropane was obtained.

a) Calculate the theoretical yield of product.

b) Hence, calculate the percentage yield.

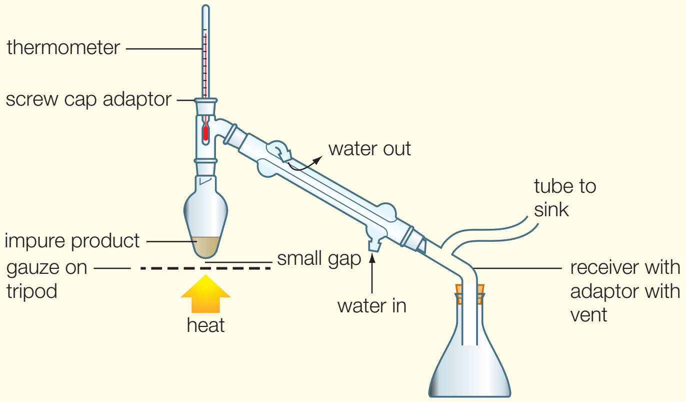


Figure 6.3.16 Distillation apparatus.

Tip

For practical guidance, refer to Practical skills sheet 8, ‘Synthesising organic liquids’, which you can access via the QR code for Chapter 6.3 on page 313.

Tip

Bumping is violent boiling which shakes the apparatus and can throw liquid from the container in which it is being heated. Adding a few fragments of porous pottery or some jagged anti-bumping granules cuts the risk of bumping by helping the bubbles of vapour to form smoothly as the liquid boils.

Oxidation by acidified potassium dichromate(VI)

All alcohols react in a similar way with phosphorus halides because they all contain the –OH functional group. However, different classes of alcohol form different products when reacted with oxidising agents such as acidified potassium dichromate(VI). A primary alcohol is oxidised to an **aldehyde** and then to a **carboxylic acid**. A secondary alcohol is oxidised to a **ketone**. There is no reaction with a tertiary alcohol.

Key terms

An **aldehyde** contains the functional group–CHO as in propanal.

A **ketone** contains the functional group C=O as in propanone.

A **carboxylic acid** contains the functional group –COOH as in propanoic acid (Figure 6.3.17).

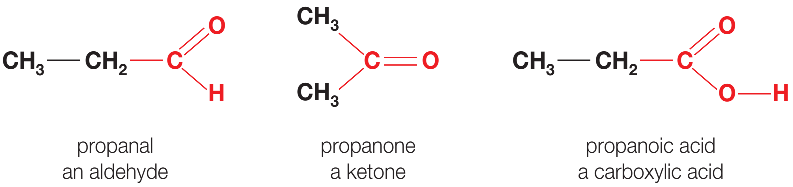

propanal
an aldehyde
propanone
a ketone
propanoic acid
a carboxylic acid

Figure 6.3.17 Propanal, propanone and propanoic acid.

Oxidation of a primary alcohol

This takes place in two steps. In the first step, an aldehyde is formed (Figure 6.3.18). If this is the required product, the apparatus used is that shown in Figure 6.3.19. This arrangement allows the aldehyde to distil off as soon as it forms and prevents further oxidation of the aldehyde.

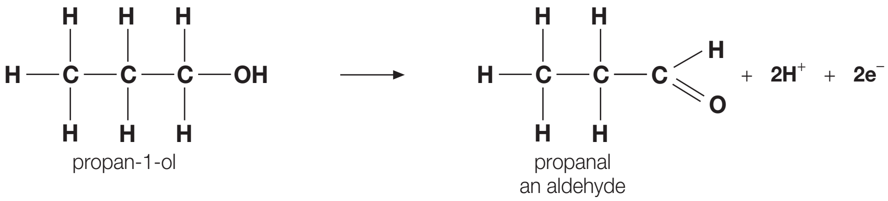

propan-1-ol
propanal
an aldehyde
+ 2H⁺ + 2e⁻

Figure 6.3.18 Oxidation of propan-1-ol to propanal by acidified $K_2Cr_2O_7$. The oxidising agent takes away the electrons (Section 3.2).

This oxidation can also be represented as a simplified equation, where [O] represents the oxidising agent:

$$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$$

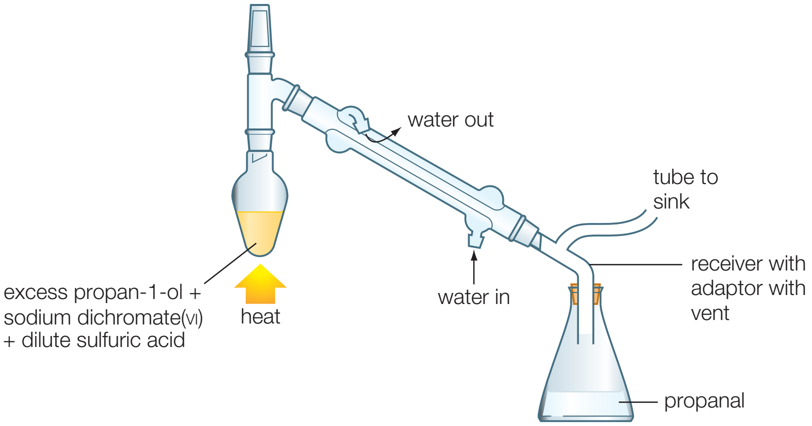

water out
tube to
sink
receiver with
adaptor with
vent
water in
excess propan-1-ol +
sodium dichromate(VI)
+ dilute sulfuric acid
heat
propanal

Figure 6.3.19 Apparatus used to oxidise a primary alcohol to an aldehyde. The aldehyde distils off as it forms.

In the second stage, the aldehyde is oxidised further to a carboxylic acid (Figure 6.3.20). If a carboxylic acid is the required product, the primary alcohol is heated with the oxidising agent and a reflux condenser is used (Figure 6.3.21). The reflux condenser ensures that any volatile aldehyde condenses and flows back into the flask, where excess oxidising agent ensures complete conversion into the carboxylic acid.

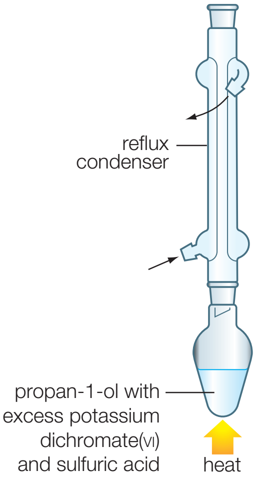

reflux condenser
propan-1-ol with excess potassium dichromate(VI) and sulfuric acid
heat

Figure 6.3.21 Apparatus used to oxidise a primary alcohol to a carboxylic acid. The reflux condenser ensures that any volatile aldehyde condenses and flows back into the flask, where excess oxidising agent ensures complete conversion.

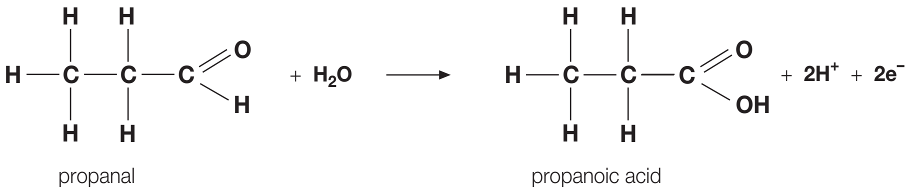

+ H_2O
+ $2H^+$ + $2e^-$
propanal
propanoic acid

Figure 6.3.20 Oxidation of propanal to propanoic acid. Oxidation is completed when a primary alcohol is heated with acidified potassium dichromate(VI) in the apparatus shown in Figure 6.3.21. This converts the alcohol first to an aldehyde, then to a carboxylic acid.

A simplified equation for the second step is

$$CH_3CH_2CHO + [O] \rightarrow CH_3CH_2COOH$$

Oxidation of a secondary alcohol

This produces a ketone (Figure 6.3.22).

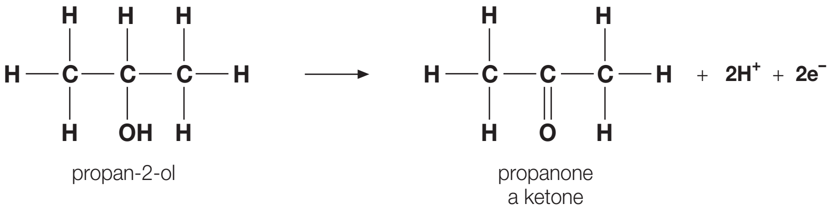

+ $2H^+$ + $2e^-$
propan-2-ol
propanone
a ketone

Figure 6.3.22 Oxidation of propan-2-ol produces propanone, a ketone.

Distinguishing between types of alcohol

An acidified solution of potassium dichromate(VI) is orange. It turns green on warming with primary or secondary alcohols as the orange colour of $Cr_2O_7^{2-}$(aq) turns to the green colour of Cr^{3+}(aq).

Tertiary alcohols do not change the colour of acidified potassium dichromate(VI), so can easily be distinguished from primary and secondary alcohols which do (Figure 6.3.23).

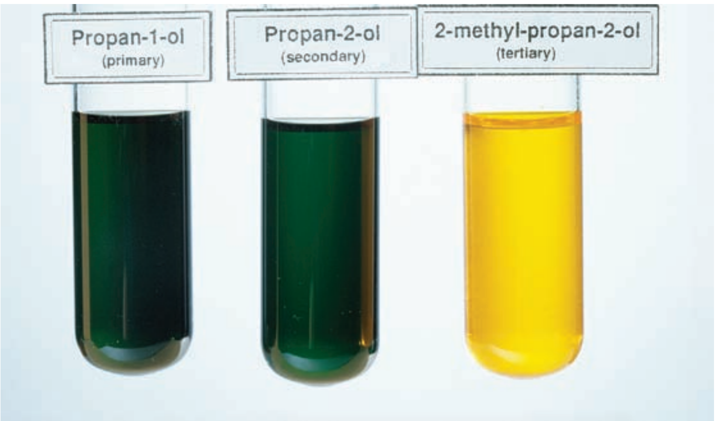

Propan-1-ol
(primary)
Propan-2-ol
(secondary)
2-methyl-propan-2-ol
(tertiary)

Figure 6.3.23 The result of warming three alcohols with an acidic solution of potassium dichromate(VI). Dichromate(VI) ions are reduced to green chromium(III) ions if there is a reaction. Tertiary alcohols do not react with potassium dichromate(VI).

However, this reaction does not distinguish between primary and secondary alcohols so a further test is needed. This is carried out on the oxidation products, the aldehydes and ketones, formed by the alcohols.

Aldehydes formed from primary alcohols can easily be oxidised further to carboxylic acids. Ketones are not easily oxidised.

So, using mild oxidising agents, such as Fehling's solution or Benedict's solution, it is possible to distinguish between aldehydes and ketones and, hence, between the alcohols which formed them.

Tip

Mild oxidising agents are used to make sure there is no oxidation of ketones at all. Strong oxidising agents may cause some oxidation of ketones by breaking carbon–carbon bonds.

Distinguishing between aldehydes and ketones

Fehling's reagent does not keep, so it is made when required by mixing two solutions. One solution is copper(II) sulfate in water. The other is a solution of 2,3-dihydroxybutanedioate (tartrate) ions in strong alkali. The 2,3-dihydroxybutanedioate ions form a complex with copper(II) ions so that they do not precipitate as copper(II) hydroxide with the alkali.

Benedict's solution is similar to Fehling's solution but is more stable. It is less strongly alkaline and does not react so reliably with all aldehydes.

Aldehydes reduce the copper(II) ions in Fehling's, or Benedict's, solution to copper(I), which then precipitates in the alkaline conditions to give an orange-brown precipitate of copper(I) oxide (Figure 6.3.24).

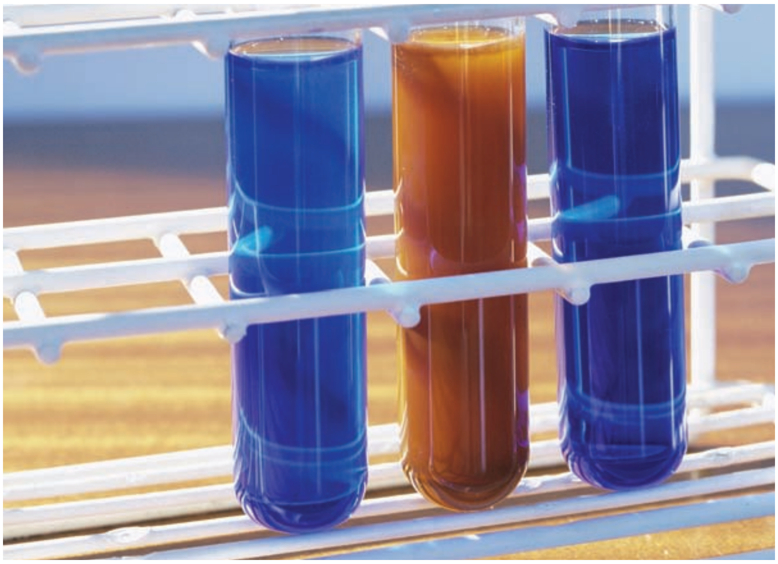


Figure 6.3.24 Fehling's reagent is used to test for aldehydes. The reagent has a blue colour as it contains copper(II) ions. The test tube in the middle contains Fehling's reagent that has been reduced by an aldehyde, to form an orange-brown precipitate of copper(I) oxide. The test tubes on the left and right contain Fehling's reagent and ketones. Ketones do not react with Fehling's reagent, hence the colour is unchanged.

Tip

Oxidation of primary or secondary alcohols occurs by loss of a hydrogen atom from the carbon atom to which the —OH group is attached. Primary alcohols have two of these hydrogen atoms so can be oxidised via aldehydes to carboxylic acids in two steps. Secondary alcohols contain one such hydrogen so can be oxidised to ketones in one step. Tertiary alcohols have no hydrogen on this atom so are not oxidised, except by powerful oxidising agents such as concentrated nitric acid which can break C—C bonds.

Tip

Infrared spectroscopy can be used to detect the functional groups in organic molecules. It is an analytical tool that can be used to show the change in functional groups when alcohols are oxidised (Section 7.2).

Core practical 5

The oxidation of ethanol

A student oxidised the primary alcohol, ethanol, to see how the choice of conditions affected the product formed according to the following instructions. The products obtained by each method were then tested and the results of the tests are shown below.

Tip

Refer to Practical skills sheet 8, 'Synthesising organic liquids'.

Part 1: Complete oxidation of ethanol

A Add 5 cm^3 water to a boiling tube. Wearing gloves, add 6 g of sodium dichromate(VI). Shake and stir to dissolve.

B Put 1.5 cm^3 ethanol into a small pear-shaped flask. Add 5 cm^3 water and a couple of anti-bumping granules. Fit a reflux condenser and clamp the apparatus ready for heating as in Figure 6.3.25.

C Taking great care, add 2 cm^3 of concentrated sulfuric acid down the condenser. Add it drop by drop from a dropping pipette.

D Then, while the mixture is still warm, begin to add the solution of sodium dichromate(VI) down the condenser. Add this solution drop by drop too – just fast enough to keep the mixture boiling without any further heating.

E When you have added all the sodium dichromate(VI) solution, heat the mixture gently with a small flame for 10 minutes.

F Stop heating and rearrange the apparatus for distillation as in Figure 6.3.26.

G Distil about 3 cm^3 into a small flask.

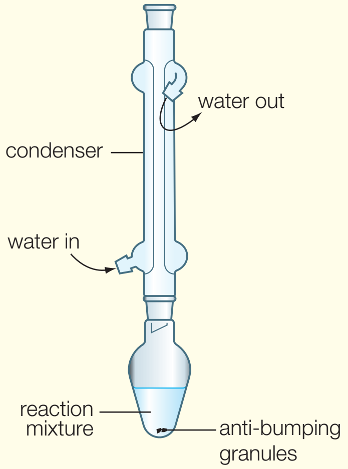


Figure 6.3.25 Apparatus for heating under reflux.

Part 2: Partial oxidation of ethanol

Now repeat the oxidation as follows using half as much of the oxidising agent as in part 1. Also allow the product to distil off as it forms.

H Add 10 cm^3 of dilute sulfuric acid to a pear-shaped flask. Wearing gloves, add 3 g sodium dichromate(VI) together with 2 or 3 anti-bumping granules.

I Add 1.5 cm^3 ethanol a few drops at a time. Shake to mix the contents until all the solid has dissolved.

J Set up the apparatus for distillation as in Figure 6.3.26. Then gently distil 2–3 cm^3 of liquid into a small flask cooled in a beaker of iced water.

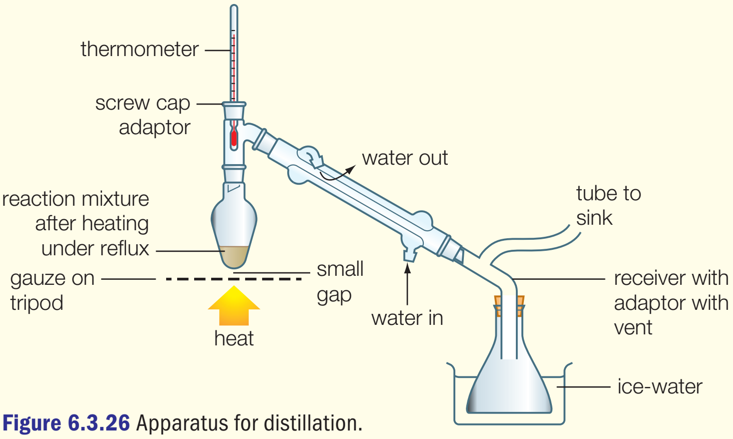


Figure 6.3.26 Apparatus for distillation.

Tests and results

Test		Observations with product from Part 1	Observations with product from Part 2
1	Carefully, note the smell of the product.	Acrid smell.	Fruitier smell.
2	Add a solution of sodium carbonate to 1 cm^3 of the distillate. Note how much of the solution you need to neutralise the sample.	Neutralises a significant quantity of the carbonate solution, giving off bubbles of gas.	Only neutralises a drop or two of sodium carbonate solution.
3	Add a few drops of the product to freshly made Fehling's solution. Heat the mixture in a hot water bath. Look for colour changes and the formation of a precipitate.	No reaction.	Reagent turns from blue to green before the main colour is a red–orange precipitate.

Questions

1 Show that the results indicate that two distinct oxidation products have been formed and identify the two products.

2 Write an equation for the reaction of sodium carbonate with the oxidation product from Part 1.

3 Name the red–orange precipitate formed in Test 3 and the oxidation product formed at the same time.

4 Write half-equations for the oxidation of ethanol
  a) to the product formed in Part 1
  b) to the product formed in Part 2.

5 **a)** By considering the structures of ethanol and the two oxidation products, list the three compounds in order of increasing boiling point and explain your order.
  b) Hence discuss the use of the condenser in the preparation of these two compounds from ethanol.

6 What precautions should be taken with the dropping pipette after it has been used to add concentrated sulfuric acid in Stage C?

7 What particular precaution should be taken during Stage F?

8 State where the clamps should be placed on the apparatus in Parts 1 and 2.

Dehydration by concentrated phosphoric acid

Alcohols can be **dehydrated** to alkenes by heating with concentrated acids such as phosphoric or sulfuric. Concentrated phosphoric acid is preferred as it gives a purer product. This is because, unlike concentrated sulfuric acid, it is not also an oxidising agent and so leads to fewer side reactions.

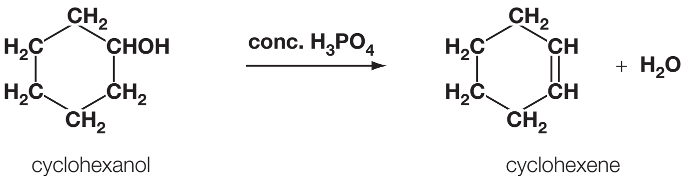


Figure 6.3.27 Dehydration of cyclohexanol to cyclohexene.

Key term

When a substance is **dehydrated** it loses water. This can be by the loss of water molecules from crystals such as $CuSO_4.5H_2O$ or by the removal of an H atom and an —OH group from adjacent atoms leading to the formation of a double bond.

An alcohol such as cyclohexanol can be heated with concentrated phosphoric acid and the alkene formed, cyclohexene, distilled off (Figure 6.3.27). This is an **elimination reaction** (see also Section 6.3.4).

Test yourself

32 Use oxidation numbers to show that it is the chromium that is reduced when $Cr_2O_7^{2-}$(aq) ions turn into Cr^{3+}(aq) ions.

33 Predict the products, if any, of oxidising the following alcohols with acidified potassium dichromate(VI):
  a) butan-1-ol when the product is distilled off immediately
  b) butan-1-ol when the reagents are heated under reflux for some time
  c) butan-2-ol
  d) 2-methylbutan-2-ol.

34 Write both half equations and simplified overall equations using [O], to show the oxidation of different alcohols to form:
  a) propanal
  b) butanoic acid
  c) cyclohexanone.

35 **a)** Write an equation for the dehydration of propan-2-ol using concentrated phosphoric acid and name the type of reaction.
  b) Dehydration of butan-2-ol forms several products. Draw and name each product.

Tip

Although knowledge of the mechanism for this reaction is not expected, it is one of several examples where removal of an —OH group occurs in acid conditions. Protonation of the —OH group occurs first so that it is actually a water molecule which is lost. H^+ is also lost from an adjacent carbon, so overall the acid acts as a catalyst.

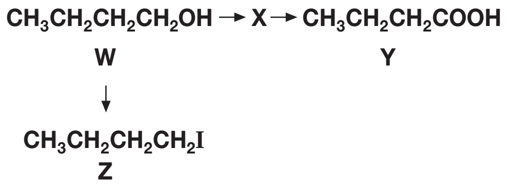
Tip

There are two common elimination reactions which form alkenes:

- the removal of water from an alcohol under acid conditions
- the removal of a hydrogen halide from a halogenoalkane under alkaline conditions.

Exam practice questions

1 Consider the following reaction scheme:



a) State the reagents and conditions needed to convert compound **W** directly to compound **Y**. *(3)*

b) Draw the structure of **X** and state how the conditions you have given in part (a) could be modified to produce compound **X** instead of **Y**. *(2)*

c) Give the reagents and conditions for converting compound **W** into compound **Z**. *(2)*

2 A few drops of a halogenoalkane were added to 2 cm^3 of ethanol in a test tube and 5 cm^3 of aqueous silver nitrate was then added. The test tube was then placed in a water bath and after a few minutes a cream precipitate had formed. This precipitate was soluble in concentrated ammonia.

a) Explain why ethanol was used in this experiment. *(2)*

b) State why the test tube containing the mixture was warmed in a water bath. *(1)*

c) Give the formula of the precipitate. Explain your answer. *(2)*

d) What can you conclude about the halogenoalkane? *(1)*

3 Draw the structure of the organic product of reacting:

a) 2-bromo-2-methylpropane under reflux with a hot solution of potassium hydroxide in ethanol *(1)*

b) 1-iodopropane with an aqueous solution of potassium hydroxide *(1)*

c) 1-bromopropane with excess ammonia in ethanol *(1)*

d) butane-1,4-diol with acidified potassium dichromate(VI) under reflux conditions *(1)*

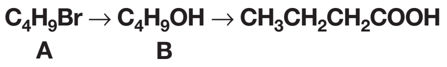
e) cyclohexanol with phosphorus(V) chloride. *(1)*

4 Propylamine can be formed either in a two-step synthesis starting from bromoethane or in a one-step synthesis starting from 1-bromopropane.

a) For each step, give the reagents and conditions and write an equation. *(10)*

b) Identify a disadvantage of each synthetic route. *(2)*

5 Consider the following synthesis of butanoic acid:

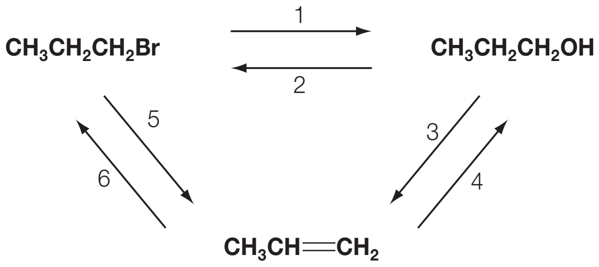


$$\underset{\mathbf{A}}{C_4H_9Br} \rightarrow \underset{\mathbf{B}}{C_4H_9OH} \rightarrow CH_3CH_2CH_2COOH$$

a) Draw displayed formulae for compounds **A** and **B**. *(2)*

b) For each step, give reagents and conditions and name the type of reaction involved. *(6)*

6 Consider the six reactions shown below.



a) For each reaction give the necessary reagent and conditions. *(11)*

b) One of the six reactions does not show formation of the major product. Identify which reaction, give the major product and explain why the product shown is not the major product. *(3)*

7 Isomers of C_4H_9Br include $CH_3CH_2CH_2CH_2Br$ and $(CH_3)_3CBr$.

Both react with aqueous potassium hydroxide to form alcohols, but the reaction mechanism is different in each case.

a) Draw the structure of the intermediate or transition state formed during each reaction and explain why the two routes are different. *(4)*

b) If $CH_3CH_2CH_2CH_2I$ were used instead, how and why would the rate of the reaction change? *(2)*

c) Draw the alternative product formed in each case if hot ethanolic potassium hydroxide were used instead. *(2)*

8 This question is about 2-bromo-3-methylbutane.

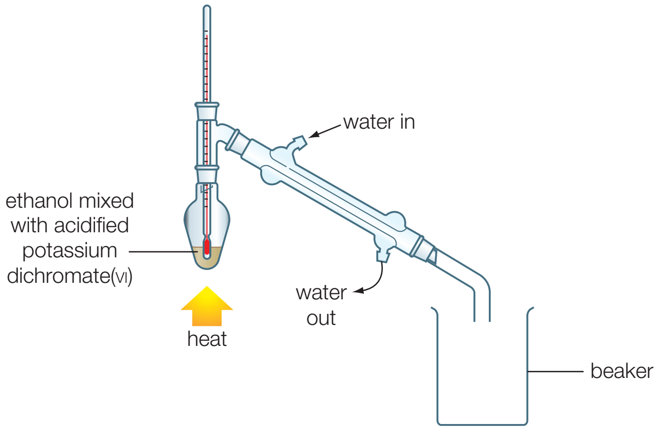
a) Give the name and formula of the product of heating 2-bromo-3-methylbutane under reflux with aqueous potassium hydroxide. Name the type of reaction taking place. *(2)*

b) Give the name and formula of the two isomers that form on heating 2-bromo-3-methylbutane under reflux with alcoholic potassium hydroxide. Name the type of reaction taking place. *(5)*

c) Give the name and formula of the product of heating 2-bromo-3-methylbutane under reflux with alcoholic ammonia. Name the type of reaction taking place. *(3)*

d) Give the name and formula of the product of heating 2-bromo-3-methylbutane under reflux with potassium cyanide in ethanol. *(2)*

9 A student attempted to prepare ethanal by oxidation of ethanol. The diagram shows the apparatus set up by the student to collect the ethanal by distillation and to measure its boiling point.



Identify three improvements that should be made to the arrangement of apparatus and give a reason for each improvement you suggest. You may assume suitable clamps are used. *(6)*

10 A sample of cyclohexene was prepared by the dehydration of cyclohexanol using concentrated phosphoric acid. The reaction mixture was distilled and the distillate obtained contained both cyclohexene and water.

Describe how acidic impurities can be removed from the distillate and a sample of dry cyclohexene obtained.

The density of cyclohexene is $0.81\,g\,cm^{-3}$. *(6)*

11 a) $11\,cm^3$ of propan-2-ol (density $0.78\,g\,cm^{-3}$) are oxidised with sodium dichromate(VI) in dilute sulfuric acid. After separating and purifying the product, this preparation produces an 80% yield. Name the product, state how it is separated and calculate the mass of pure product obtained. *(4)*

b) $9.25\,cm^3$ of butan-1-ol (density $0.81\,g\,cm^{-3}$) are heated with an excess of red phosphorus and iodine. After separating and purifying the product, this preparation produces an 85% yield. Name the product and calculate the mass of pure product obtained. *(4)*

12 Pentan-1-ol reacts with sodium to form compound **P** ($C_5H_{11}ONa$) and hydrogen gas according to the equation:

$$2CH_3CH_2CH_2CH_2CH_2OH + 2Na \rightarrow 2CH_3CH_2CH_2CH_2CH_2ONa + H_2$$

Reaction of **P** with bromomethane forms compound **Q** ($C_6H_{14}O$) which has a much lower boiling point than pentan-1-ol.

Reaction of **P** with bromoethane forms a similar compound **R** ($C_7H_{16}O$) and in a competing reaction also forms ethene.

a) Give a structural formula for **Q**. *(1)*

b) i) Name and outline a mechanism for the reaction between **P** and bromomethane. *(3)*

ii) Explain why **Q** has a much lower boiling point than pentan-1-ol. *(2)*

c) i) Give a structural formula for **R**. *(1)*

ii) Explain how **P** can react with bromoethane to form ethene and name the type of reaction involved. *(3)*

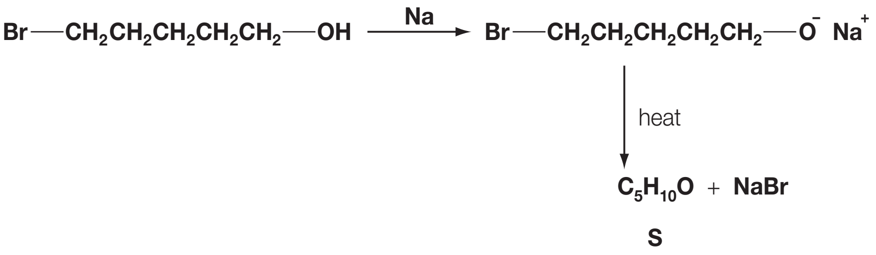
d) Consider the reaction sequence to form the cyclic compound **S** ($C_5H_{10}O$) below.

i) Give a skeletal formula for **S**. *(1)*

ii) Explain how **S** is formed and name the type of reaction. *(2)*

iii) Explain why a similar sequence of reactions starting from 2-bromopentan-1-ol does not form a cyclic compound. *(2)*

iv) State with a reason whether the boiling point of **S** will be higher or lower than pentan-1-ol. *(2)*



$$\begin{tikzcd} \mathrm{Br{-}CH_2CH_2CH_2CH_2CH_2{-}OH} \arrow[r, "\mathrm{Na}"] & \mathrm{Br{-}CH_2CH_2CH_2CH_2CH_2{-}O^-\ Na^+} \arrow[d, "\mathrm{heat}"] \\ & \mathrm{C_5H_{10}O + NaBr} \end{tikzcd}$$

S

7

Modern analytical techniques I

7.1 Mass spectra of organic compounds

Tip

Tests and observations in inorganic chemistry are described in Section 5.11.

In modern chemistry, the use of instrumental techniques such as mass spectrometry for analysis is more important than chemical analysis. Although the instruments may be expensive to purchase, analysis using them is quick to perform and extremely accurate. Chemical analysis also destroys the sample by reacting it; instrumental analysis uses a very small sample and, in most cases, does not destroy it.

Mass spectrometry is an accurate technique for determining relative atomic masses (Section 1.4). Mass spectrometry can also help to determine the relative molecular masses and molecular structures of organic compounds. In this way, it can be used to identify unknown compounds. The technique is extremely sensitive and requires very small samples, which can be as small as one nanogram (10^{-9}g).

Inside a mass spectrometer (Figure 7.1) there is a very high vacuum so that it is possible to produce and study ionised molecules and fragments of molecules. The molecular fragments could not exist other than in a high vacuum.

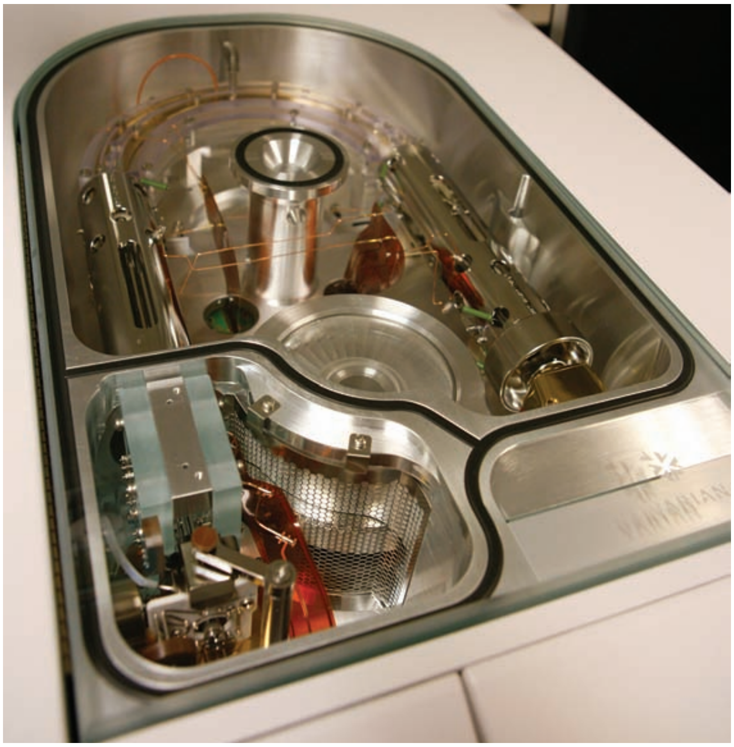


Figure 7.1 A mass spectrometer used for analysis. The sample is fed into the bottom left of the instrument where it is vaporised and ionised. The ions are accelerated along the U-shaped glass tube and steered by electric and magnetic fields to reach the gold-coloured detector on the bottom right. This part of the instrument measures about 70 cm × 50 cm.

A beam of high-energy electrons bombards the molecules of the sample (Figure 7.2). This turns them into ions by knocking out one or more electrons.

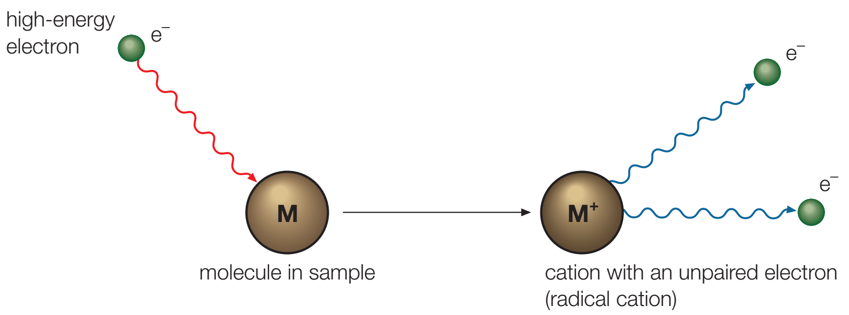

high-energy electron
e⁻
M
molecule in sample
M⁺
e⁻
e⁻
cation with an unpaired electron (radical cation)

Figure 7.2 High-energy electrons ionising a molecule in a mass spectrometer. Knocking out one electron leaves a positive ion, shown by the symbol M^+.

Bombarding molecules with high-energy electrons not only ionises them, but may also split them into fragments (Figure 7.3). As a result, the mass spectrum consists of a 'fragmentation pattern'.

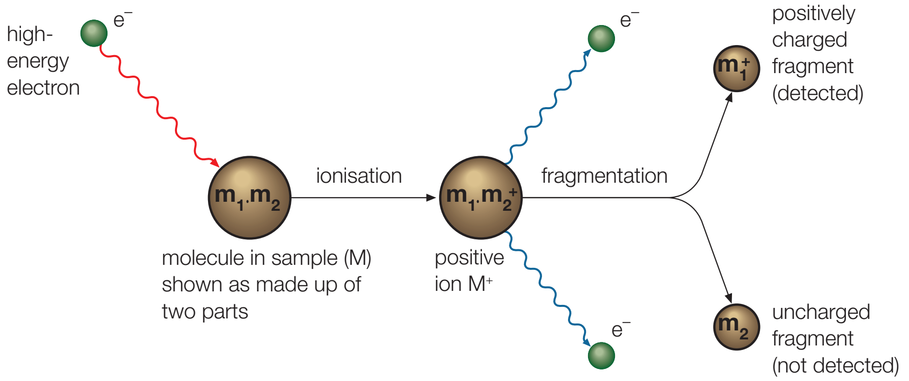

high-energy electron
e⁻
$m_1.m_2$
ionisation
molecule in sample (M) shown as made up of two parts
$m_1.m_2^+$
positive ion M⁺
e⁻
e⁻
fragmentation
m_1^+
positively charged fragment (detected)
m_2
uncharged fragment (not detected)

Figure 7.3 Ionisation and fragmentation of a single molecule $m_1.m_2$ which fragments into two parts m_1^+ and m_2. Only charged species show up in the mass spectrum because electric and magnetic fields have no effect on neutral fragments. So, in this case, the instrument only detects m_1^+.

Molecules break up more readily at weak bonds, or at bonds which give rise to more stable fragments. It turns out that positive ions with the charge on a secondary or tertiary carbon atom are more stable than ions with the charge on a primary carbon atom. Species such as CH_3CO^+ are also more stable where a bond breaks adjacent to the C=O double bond.

After ionisation and fragmentation, the charged species are accelerated and deflected by electric and magnetic fields. The extent of the deflection depends on the ratio of the mass of the fragment to its charge, its **mass-to-charge ratio (*m/z*)**. The number of charges (1, 2 and so on) is called *z*, but in most of the examples you will meet $z = 1$.

The positive ions finally reach a detector where they cause a small current. This is amplified and the signal fed to a computer.

Key term

The **mass-to-charge ratio** (*m/z*) is the ratio of the relative mass of an ion to its charge.

The output from the detector of a mass spectrometer is often present as a 'stick diagram' (see Figure 7.4). This shows the strength of the signal produced by ions of varying mass to charge ratio. The scale on the vertical axis shows the relative abundance of the ions. The horizontal axis shows the *m*/*z* values.

When analysing molecular compounds, the peak with the largest *m*/*z* value is usually the ionised whole molecule. So the mass of this '**molecular ion**' or 'parent ion', *M*, is the relative molecular mass of the compound.

Key term

The **molecular ion** (also called parent ion) is the positive ion, M^+, formed when a molecule loses one electron. This species is also a radical since one electron has been lost from a pair in the molecule, leaving one unpaired electron.

Tip

Recently, alternative less expensive mass spectrometers have been developed. These involve alternative ionisation techniques (such as electrospray ionisation) and alternative mass analysers which use quadrupoles instead of magnetic fields or measure time of flight. (Your examination will not test these alternative methods.)

The existence of isotopes shows up in mass spectra. For instance, bromine exists as the isotopes ^{79}Br and ^{81}Br in almost equal amounts. The spectrum of bromoethane (Figure 7.4) shows two molecular ion peaks at *m*/*z* = 108 and 110 of almost equal abundance. Fragmentation of either molecular ion (Figure 7.5) first involves breaking of the C–Br bond to produce the fragment ion $C_2H_5^+$ with *m*/*z* = 29. Further successive loss of hydrogen atoms forms ions which produce the peaks at *m*/*z* = 28, 27 and 26.

Tip

Take care when describing the peak for the molecular ion. Do not simply use the word highest to describe the peak because highest could be confused with tallest, which applies to the most abundant ion.

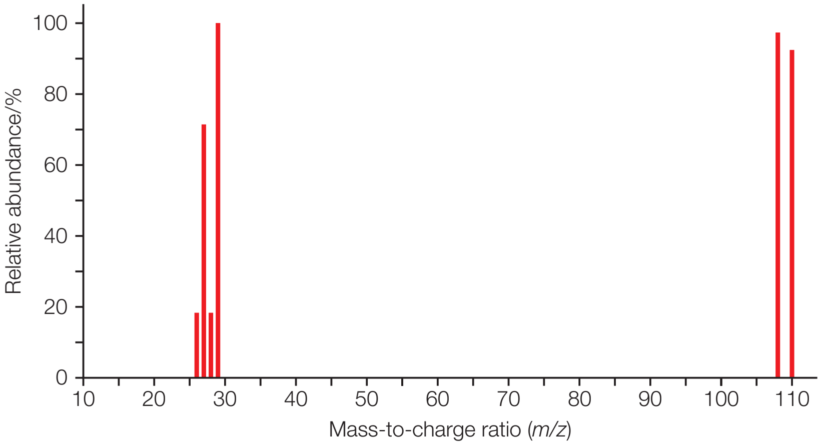


Figure 7.4 The mass spectrum of bromoethane. There are two molecular ion peaks because of the presence of two isotopes of bromine.

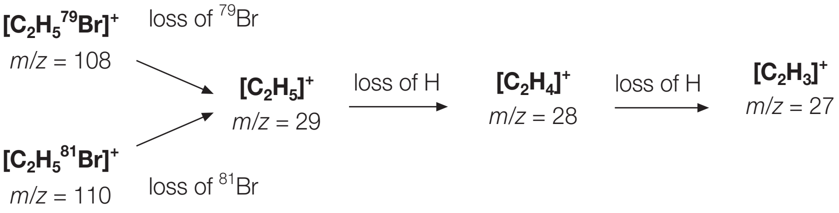


Figure 7.5 Fragmentation of the molecular ions of bromoethane.

Chemists study mass spectra in order to gain insight into the structure of molecules. They identify the fragments from their relative masses, and then piece together likely structures, sometimes with the help of evidence from other methods of analysis, such as infrared spectroscopy. The example on page 228 shows use of mass spectrometry to identify a compound.

Example

The mass spectrum in Figure 7.6 is known to be that of ethyl propanoate, $CH_3CH_2COOCH_2CH_3$ or methyl butanoate, $CH_3CH_2CH_2COOCH_3$. Use the spectrum to identify which of the two isomers produced the spectrum.

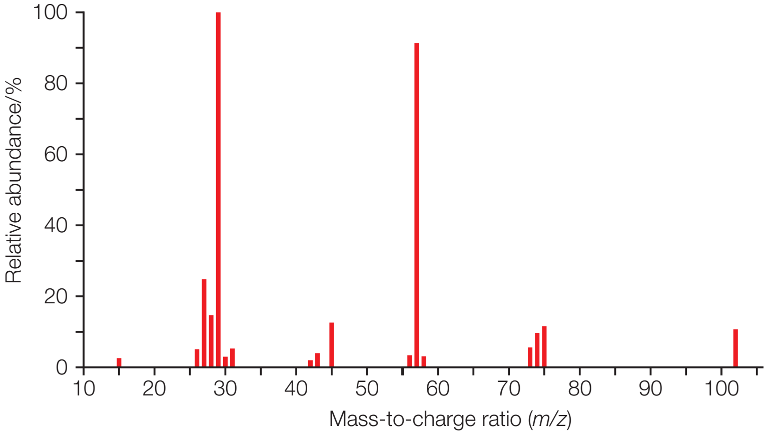


Figure 7.6 Mass spectrum of an isomer of $C_5H_{10}O_2$.

Answer

The spectrum shows a molecular ion peak at $m/z = 102$. Both isomers have molecular formula $C_5H_{10}O_2$ so both would have a molecular ion peak at $m/z = 102$.

The other main peaks shown are at $m/z = 57$ and $m/z = 29$.

Ethyl propanoate can produce a peak at $m/z = 57$ for the fragment ion $CH_3CH_2CO^+$ and a peak at $m/z = 29$ for the fragment ion $CH_3CH_2^+$. Both of these peaks correspond to fragment ions formed by breaking of the C–C bonds adjacent to the C=O group.

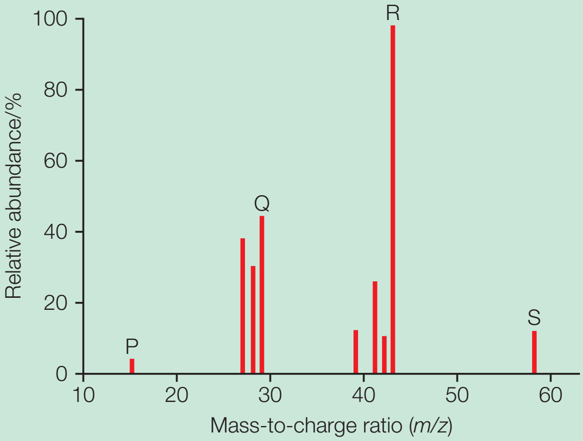
Methyl butanoate is unlikely to produce a peak at $m/z = 57$. Its major fragment peaks are likely to be at $m/z = 71$ for the ion $CH_3CH_2CH_2CO^+$ or at $m/z = 43$ for $CH_3CH_2CH_2^+$. Neither of these values correspond to major peaks in the given spectrum.

The evidence indicates that the compound is ethyl propanoate.

Test yourself

1 The mass spectrum of butane, C_4H_{10}, is shown on the right.

- **a) i)** Which peak in the mass spectrum of butane corresponds to the molecular ion?
  - **ii)** What is the relative mass of this ion?
- **b)** Suggest the identity of the fragments labelled P, Q and R.
- **c)** Suggest a reason why the peak at $m/z = 15$ is relatively weak.
- **d)** Use symbols to show one way in which the parent ion of butane could fragment.



7.2 Infrared spectroscopy

Spectroscopy is a term which covers a range of practical techniques for studying the composition, structure and bonding of compounds. Spectroscopic techniques are now the essential 'eyes' of chemistry and have many uses in detection and measurement.

The range of techniques available covers many parts of the electromagnetic spectrum – including the infrared, visible and ultraviolet regions. The instruments used are called either spectroscopes, which emphasises the use of techniques for making observations, or spectrometers, which emphasises the importance of measurements.

Infrared spectroscopy (or IR spectroscopy) is an analytical technique used to identify functional groups in organic molecules. Infrared radiation from a glowing lamp or fire makes us feel warm. This is because infrared frequencies correspond to the natural frequencies of vibrating atoms in molecules. Our skin warms up as the molecules absorb infrared and vibrate faster.

Most compounds absorb infrared radiation. A sample in a spectrometer (Figure 7.7) absorbs infrared radiation at wavelengths which correspond to the natural frequencies at which vibrating bonds in the molecules bend and stretch. However, it is only molecules that change their polarity as they vibrate which interact with IR. The absorptions are detected, analysed and the **absorption spectrum** displayed by a computer or printed (Figure 7.8). The absorption spectrum is a plot of **transmittance** against **wavenumber**.

Figure 7.7 Using an infrared spectrometer. The instrument covers a range of infrared wavelengths and a detector records how strongly the sample absorbs at each wavelength. Wherever the sample absorbs, there is a dip in the intensity of the radiation transmitted which shows up as a dip in the plot of the spectrum.

Test yourself

2 Put the following stages in order during mass spectrometry: acceleration, fragmentation, ionisation, deflection according to m/z, detection, vaporisation.

3 Give two reasons why it is important to have a high vacuum inside a mass spectrometer.

4 Propan-1-ol and propan-2-ol are position isomers. Suggest which has a major peak in its mass spectrum at $m/z = 31$ and predict a major fragmentation peak in the spectrum of the other isomer. Explain your answers.

Key terms

An **absorption spectrum** is a plot showing how strongly a chemical absorbs radiation over a range of frequencies.

Transmittance on the vertical axis of infrared spectra measures the percentage of radiation which passes through the sample. The troughs appear at those wavenumbers where the compound absorbs strongly. Chemists often refer to these dips in the line as 'peaks' because they indicate high levels of absorption.

Infrared **wavenumbers** range from 400 to 4500 cm^{-1}. The wavenumber is the number of waves in 1 cm. Spectroscopists find the numbers more convenient than wavelengths.

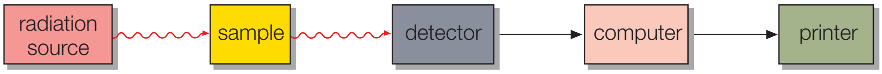

radiation source
sample
detector
computer
printer

Figure 7.8 Essential features of a modern single-beam spectrometer.

Bonds vibrate in particular ways and absorb radiation at specific wavelengths. This means that it is possible to look at an infrared spectrum and identify particular functional groups. Figure 7.9 shows, on the left, a diatomic molecule stretching and, on the right, a V-shaped molecule bending.

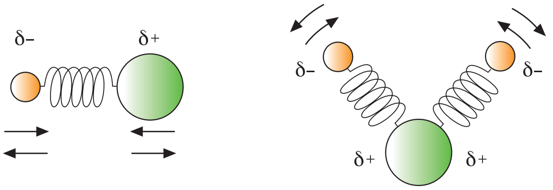


Figure 7.9 Bond vibrations give rise to absorptions in the infrared region. Vibrations of molecules which cause a fluctuating polarity interact with electromagnetic waves.

Tip

Only molecules which change polarity as they vibrate will absorb IR. Polar molecules such as CO always absorb. Non-polar molecules such as N_2 or O_2 never absorb, but some non-polar molecules such as CO_2 will absorb as some stretching or bending vibrations can cause a change in polarity (Figure 7.10).

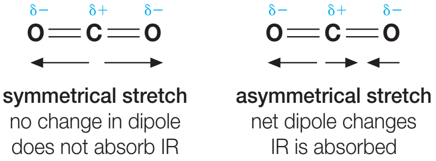

δ−
δ+
δ−
O═C═O
symmetrical stretch
no change in dipole
does not absorb IR
δ−
δ+
δ−
O═C═O
asymmetrical stretch
net dipole changes
IR is absorbed

Figure 7.10 Symmetrical and asymmetrical stretching vibrations of carbon dioxide.

Spectroscopists have found that it is possible to correlate absorptions in the region 4000 to 1500 cm^{-1} with the stretching or bending vibrations of particular bonds. As a result, infrared spectra give valuable clues about the presence of functional groups in organic molecules. The important correlations between different bonds and observed absorptions are shown in Figure 7.11.

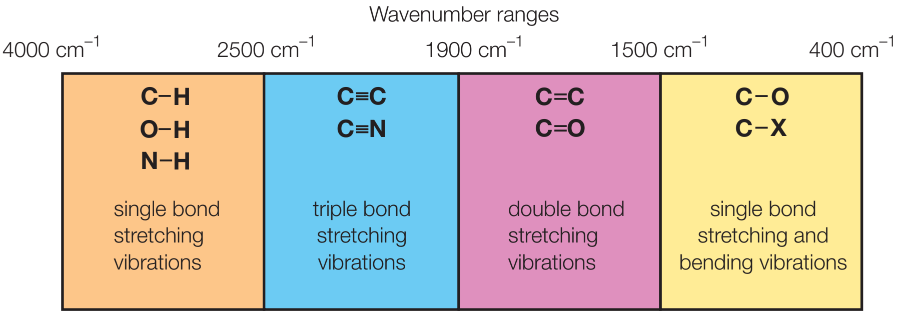

Wavenumber ranges
4000 cm⁻¹
2500 cm⁻¹
1900 cm⁻¹
1500 cm⁻¹
400 cm⁻¹
C–H
O–H
N–H
single bond stretching vibrations
C≡C
C≡N
triple bond stretching vibrations
C=C
C=O
double bond stretching vibrations
C–O
C–X
single bond stretching and bending vibrations

Figure 7.11 The main regions of the infrared spectrum and important correlations between bonds and observed absorptions.

However, the strength of a particular bond varies in different molecules because of the effect of different atoms or groups next to the bond. Data on bond strengths are usually given as mean bond enthalpies which take into account the different environments. For the same reasons, infrared absorption wavenumbers of particular bonds are usually quoted as a range of values. In some cases more specific ranges are listed and this enables different molecules to be identified (see the infrared spectroscopy data sheet in the Edexcel Data booklet). For example, the C=O stretching vibrations distinguish between aldehydes (1740 to 1720 cm^{-1}) and ketones (1720 to 1700 cm^{-1}), and the O–H stretching vibrations distinguish between alcohols and phenols (3750 to 3200 cm^{-1}) and carboxylic acids (3300 to 2500 cm^{-1}).

The example shows the use of infrared spectra to identify compounds.

Tip

Hydrogen bonding broadens the absorption peaks of –OH groups in alcohols, and even more so in carboxylic acids, where the O–H absorption also overlaps with the C–H absorption.

Example

Compounds P and Q are isomers with molecular formula $C_4H_{10}O$.

P has an absorption peak in its infrared spectrum at 3355 cm^{-1}. Q has an absorption peak at 3337 cm^{-1}

When P was heated with acidified potassium dichromate(VI), the colour of the mixture changed from orange to green. The organic compound formed was distilled off and was found to have an absorption peak in its infrared spectrum at 1718 cm^{-1}.

When Q was heated with acidified potassium dichromate(VI), the orange colour did not change.

Identify compounds P and Q.

Answer

The absorption peaks at 3355 and 3337 cm^{-1} show the presence of the O–H functional group, so both compounds are alcohols.

Reaction with acidified potassium dichromate(VI) oxidised P. The absorption at 1718 cm^{-1} in the spectrum of the oxidation product shows the presence of a ketone C=O bond, rather than an aldehyde C=O bond which would have absorbed between 1740 and 1720 cm^{-1}.

Therefore, the oxidation product must have been butanone, $CH_3CH_2COCH_3$, and P must be butan-2-ol, $CH_3CH_2CH(OH)CH_3$.

When Q was heated with the oxidising agent, no reaction occurred.

So Q must be a tertiary alcohol and is, therefore, 2-methylpropan-2-ol, $(CH_3)_3COH$.

Molecules with several atoms can vibrate in many ways because the vibrations of one bond affect others close to it. The region between 1500 cm^{-1} and 400 cm^{-1} contains absorptions for some single bond stretching vibrations as well as many bending vibrations. This leads to a very complex pattern in which it is difficult to identify individual absorptions.

However, this complexity is useful because the unique absorption pattern here can be used as a ‘fingerprint’ to identify a particular compound, and so this is called the **fingerprint region** of the spectrum. The complex pattern for an unknown compound can be compared with recorded infrared spectra in a database. An exact match will identify the unknown compound.

Infrared spectroscopy is an analytical tool that can be used to monitor the progress of an organic synthesis. Comparing the spectrum of the final product with the known spectrum in a database can be used to check if the product is pure.

Key term

The **fingerprint region** is the complex region of the spectrum below 1500 cm^{-1} which contains many single bond stretching and bending vibrations and is unique to each molecule.

Tip

Infrared spectra are unique in giving information about the absence of functional groups. If a characteristic absorption is not present in the spectrum, then the functional group which would cause it cannot be present in the molecule.

Test yourself

5 Why do the vibrations of O–H, C–O and C=O bonds show up strongly in infrared spectra, while C–C vibrations do not?

6 Figure 7.12 shows the infrared spectra of ethanol, ethanal and ethanoic acid.

- **a)** Which vibrations give rise to the peaks marked with the letters A–G?
- **b)** Which spectrum belongs to which compound?
- **c)** Why do two of the spectra have broad peaks at wavenumbers between 3000 and 3500 cm^{-1}?

7 The infrared spectrum of a sample of propanal prepared by oxidation of propan-1-ol contained a weak absorption at 3437 cm^{-1}. Suggest two possible reasons for the appearance of this absorption.

8 Suggest reasons why it is better to use infrared spectroscopy to check the purity of a liquid product from a synthesis than to measure its boiling temperature.

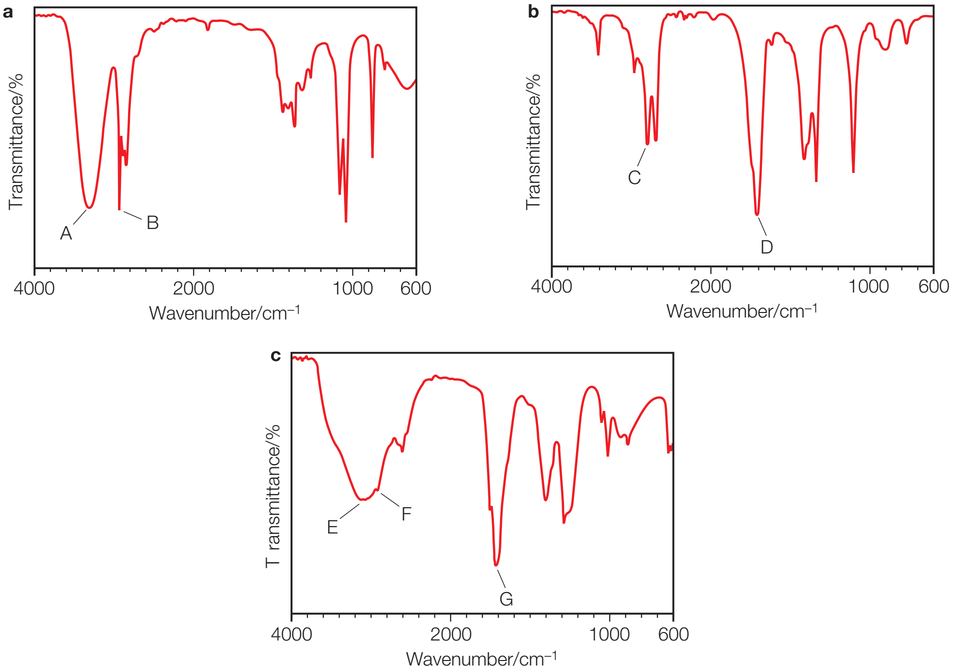


Figure 7.12 Infrared spectra for three organic compounds.

Core practical 7 (part 2)

Analysis of some organic unknowns

Bottles of six organic compounds have lost their original labels so have been re-labelled with the letters P, Q, R, S, T and U. The compounds are known to be hexane, hex-1-ene, hexan-2-ol, hexanal, hexanoic acid and 2-bromohexane.

A student carried out a series of test-tube reactions to identify each compound. The tests are described below.

To interpret the results, you will need to refer to the data sheet 'Characteristic reactions of organic functional groups', which you can access via the QR code for Chapter 7 on page 313. For Question 11, you will also need to refer to the infrared spectroscopy data sheet from the Edexcel Data booklet.

Test A

Each of the six compounds was warmed in a separate test tube with acidified potassium dichromate(VI) solution. Compounds R and U turned the colour of the solution from orange to green but the other four compounds had no effect.

1 Identify which of the compounds could be R or U.
2 State how the test tubes were warmed and give a reason for this method.

Test B

Samples of R and U were separately added to test tubes containing Fehling's solution. U gave a positive test but R did not.

3 Describe how Fehling's test was carried out, including any precautions necessary.
4 State what was observed to indicate a positive Fehling's test and hence identify R and U.

Test C

Sodium hydrogencarbonate solution was added to compounds P, Q, S and T. Q gave a positive result but P, S and T did not react.

5 Describe what was observed when Q reacted with sodium hydrogencarbonate solution.
6 Identify Q and write an equation for its reaction with sodium hydrogencarbonate solution.

Test D

Bromine water was added drop-wise to samples of P, S and T. Only P reacted.

7 Describe what was seen when P reacted with bromine water.
8 Identify P and write an equation for the reaction of P with bromine water to form the major product.

Test E

Samples of S and T were warmed with aqueous silver nitrate in ethanol. Only T gave a positive test.

9 Describe what was seen when T reacted with aqueous silver nitrate in ethanol.
10 Identify S and T and write equations for the reactions occurring during Test E.
11 The infrared spectra of the compounds were compared.
    a) Give the wavenumber of one absorption each in the spectra of hex-1-ene, hexan-2-ol, hexanal and hexanoic acid which could be used to identify these compounds.
    b) Suggest how hexane and 2-bromohexane could be positively identified using their infrared spectra but without referring to one single absorption.

Tip

Analysis of inorganic unknowns is covered in Core practical 7 (part 1), in Chapter 5.

Tip

For practical guidance, refer to Practical skills sheet 9, 'Analysing organic unknowns', which you can access via the QR code for Chapter 7 on page 313.

Exam practice questions

Where relevant, use the infrared spectroscopy data sheet from the Edexcel Data booklet to help you answer these questions.

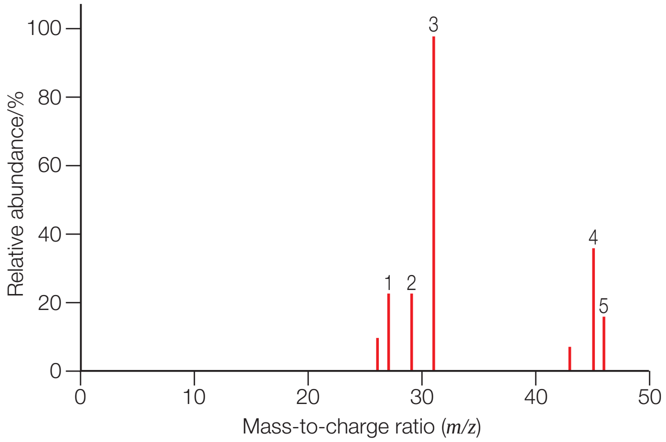
1 The mass spectrum of ethanol is shown below.

a) Match the numbered peaks with the formulae of these positive ions from ethanol molecules in a low pressure mass spectrometer: $C_2H_5^+$, CH_2OH^+, $C_2H_5O^+$, $C_2H_5OH^+$, $C_2H_3^+$. *(3)*

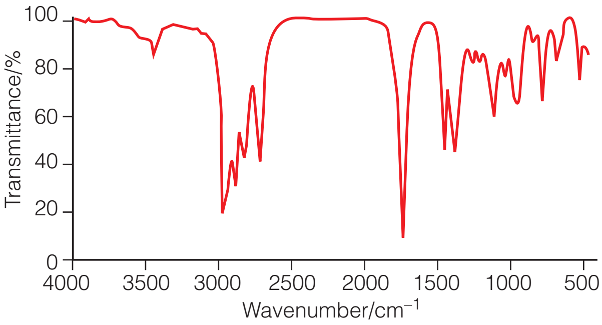
b) Write an equation to represent the formation of the molecular ions. *(2)*

c) i) Write an equation to show how the molecular ion fragments to give CH_2OH^+. *(2)*

ii) Why does the other chemical species formed during this fragmentation process not show up in the mass spectrum? *(2)*



2 Oxidation of an alcohol with formula C_4H_9OH gives a product with the infrared spectrum shown below. Use the infrared spectroscopy data sheet from the Edexcel Data booklet to interpret the spectrum. State the reagents and conditions used to carry out the oxidation of the alcohol, giving your reasons, and suggest two possible structures for the alcohol. *(6)*



3 The existence of isotopes shows up in the mass spectrum of organic compounds. The existence of the two chlorine isotopes ^{35}Cl and ^{37}Cl can be detected in the spectra of chloroalkanes.

a) i) Explain why the mass spectrum of chloroethane has peaks with m/z values of 64 and 66. *(1)*

ii) Why is the ion with an m/z value of 64 about three times as abundant as the ion with the m/z value of 66? *(1)*

b) Account for these facts about the mass spectrum of dichloroethene.

i) Although the M_r of dichloroethene is 97 there is no peak in the mass spectrum at $m/z = 97$. *(2)*

ii) It includes three peaks at m/z values of 96, 98 and 100 with intensities in the ratio 9 : 6 : 1. *(3)*

iii) It includes two peaks at m/z values of 61 and 63 with intensities in the ratio of 3 : 1. *(2)*

4 High resolution mass spectrometers can measure relative molecular masses to four decimal places. The M_r of a compound was found to be 72.0625. Compounds with molecular formulae C_5H_{12}, C_4H_8O and $C_3H_4O_2$ all have M_r values of 72 to the nearest whole number.

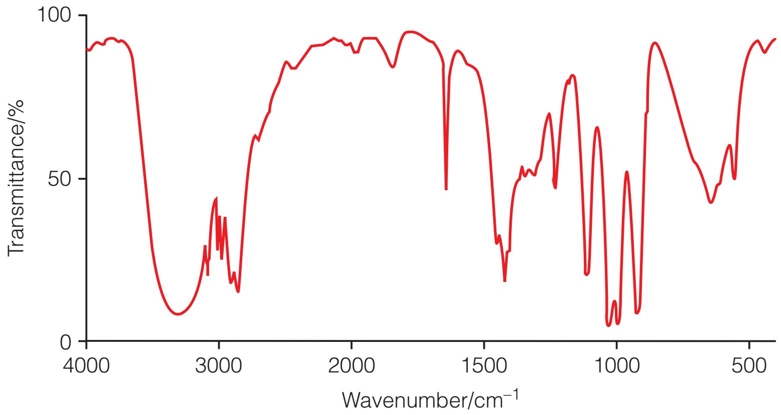
a) Use the precise relative atomic masses given to identify the correct molecular formula for this compound. *(2)*

Element	Relative atomic mass
hydrogen	1.0079
carbon	12.0107
oxygen	15.9994

b) When added to aqueous sodium carbonate, the compound reacted to give an effervescence. Suggest a structure for the compound. *(2)*

5 Three isomeric compounds with molecular formula C_3H_6O were studied using infrared spectroscopy and mass spectrometry.

Compounds **A** and **B** both had absorptions in their IR spectra at about 1720 cm^{-1}. The IR spectrum of **C** is shown below.

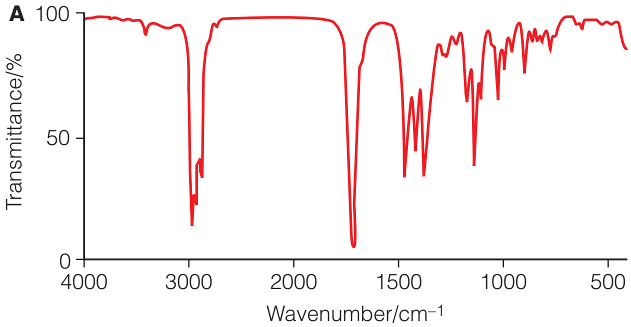


The mass spectrum of **A** had major peaks at $m/z = 58$, 43 and 15, **B** had major peaks at $m/z = 58$ and 29 and **C** had major peaks at $m/z = 58$, 57 and 31.

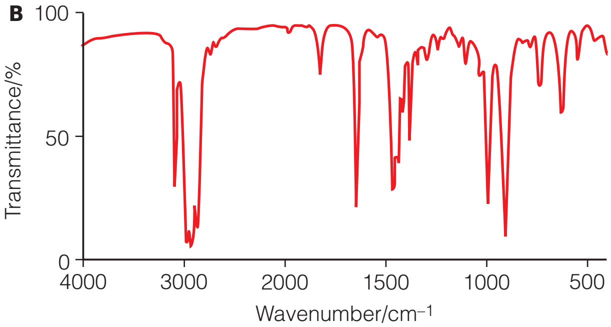
Suggest structures for the three compounds and explain your answer. *(9)*

6 Five compounds were studied using infrared spectroscopy: hexan-1-ol, hexan-3-one, hexanoic acid, hex-1-ene and 1-chlorohexane. IR spectra of four of these compounds are shown below.

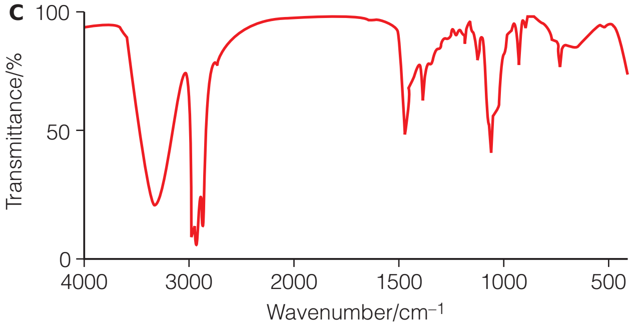
A



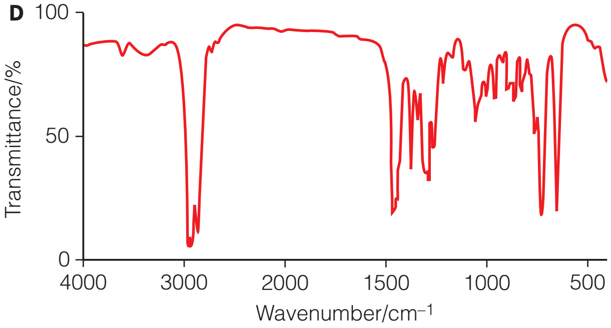
B



C



D



a) Use the infrared spectroscopy data sheet from the Edexcel Data booklet to identify which spectrum corresponds to which compound. *(4)*

b) Give reagents and conditions for the conversion of:

i) 1-chlorohexane into hexan-1-ol and name the mechanism of the reaction *(3)*

ii) hexan-1-ol into hexanal. State how you could use IR spectroscopy to show that the reaction was complete. *(3)*

7 An organic compound **X** contains the elements carbon, hydrogen and oxygen only. Analysis showed that it contains 54.5% carbon and 9.1% hydrogen by mass. The mass spectrum showed a molecular ion peak at $m/z = 88$ and a fragmentation peak at $m/z = 43$. IR peaks were observed at 3408 cm^{-1} and 1709 cm^{-1}.

When **X** was heated under reflux with acidified potassium dichromate(VI), a product **Y** was formed. The IR spectrum of **Y** contained a broad peak at 3087 cm^{-1}.

Deduce the structure of compounds **X** and **Y** and explain your deductions. *(11)*

8

Energetics I

8.1 Energy changes

Thermochemistry is the study of energy changes in chemistry. With the help of thermochemistry, chemists can decide whether or not reactions are likely to occur and explain the stability of compounds. Energy changes from chemical reactions are also of great practical importance. The energy changes during burning are crucial to the fuel and food industries. The prices of fuels are closely related to their energy values and dieticians give advice related to their knowledge of energy-providing foods

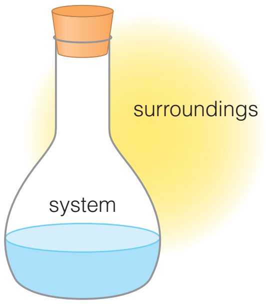


Figure 8.1 A system and its surroundings.

In thermochemistry, the term 'system' is important and it has a precise meaning. It describes just the material or the mixture of chemicals being studied. Everything around the system is called the surroundings (Figure 8.1). The surroundings include the apparatus, the air in the laboratory – in theory everything else in the Universe.

In a closed system like that in Figure 8.1, the system cannot exchange matter with its surroundings because the flask is closed with a bung. It can, however, exchange energy with the surroundings. If the bung is removed, the system is described as 'open'. An open system can exchange both energy and matter with its surroundings.

Whenever a change occurs in a system, there is almost always an energy change involving transfer of energy between the system and its surroundings. The energy transferred between a system and its surroundings is described as an **enthalpy change** when the change happens at constant pressure. The symbol for an enthalpy change is ΔH and its units are $\mathrm{kJ\,mol^{-1}}$.

Key term

An **enthalpy change**, ΔH, is the overall energy exchanged with the surroundings when a change happens at constant pressure and the final temperature is the same as the starting temperature.

Tip

Scientists use the capital Greek letter 'delta', Δ, for a change or difference in a physical quantity. So, ΔH means change in enthalpy and ΔT means change in temperature.

8.2 Enthalpy changes

Exothermic changes

Exothermic changes give out energy that often just heats up the surroundings. Burning is an obvious exothermic chemical reaction. Respiration is another exothermic reaction in which foods are oxidised to provide energy for living things to grow, move and keep warm. Hot packs used in self-warming drinks and in treating painful rheumatic conditions also involve exothermic reactions (Figure 8.2).

Tip

Remember: in an **ex**othermic change, energy leaves the system, just as people leave a building by the **ex**it.

Figure 8.2 A self-warming can of coffee – pressing the bulb on the bottom of the can starts an exothermic reaction in a sealed compartment. The energy released heats the coffee.

Figure 8.3 shows what happens in the exothermic reaction between calcium oxide and water. This reaction can be used in hot packs.

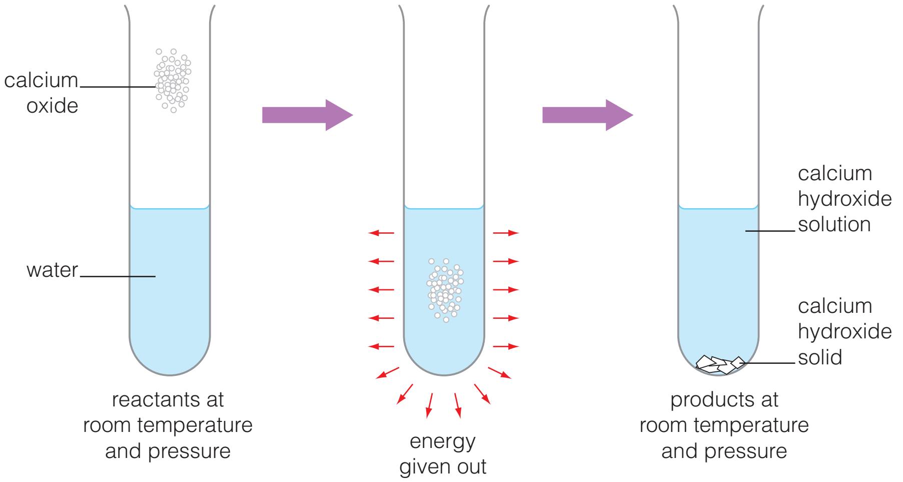

calcium oxide
water
reactants at room temperature and pressure
energy given out
calcium hydroxide solution
calcium hydroxide solid
products at room temperature and pressure

Figure 8.3 The exothermic reaction that takes place in some hot packs.

When one mole of solid calcium oxide reacts with water to form calcium hydroxide solution, 1067 kJ of energy are given out. The system loses energy by heating the surroundings. This loss of energy from the system means that ΔH is negative. The enthalpy change is often written alongside the equation for the reaction as in this example:

$$\mathrm{CaO(s)} + \mathrm{H_2O(l)} \rightarrow \mathrm{Ca(OH)_2(aq)} \quad \Delta H = -1067\,\mathrm{kJ\,mol^{-1}}$$

The energy changes in chemical reactions can be summarised in enthalpy level diagrams.

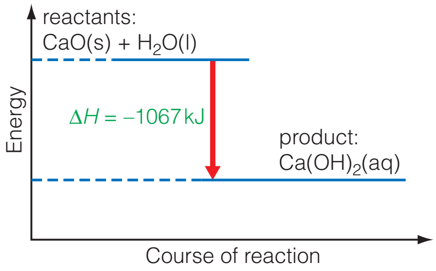

reactants:
$\mathrm{CaO(s)} + \mathrm{H_2O(l)}$
$\Delta H = -1067\,\mathrm{kJ}$
product:
$\mathrm{Ca(OH)_2(aq)}$
Energy
Course of reaction

Figure 8.4 An enthalpy level diagram for the reaction of calcium oxide with water.

Figure 8.4 shows the enthalpy level diagram for the reaction of calcium oxide with water. Energy is lost to the surroundings and, therefore, the products are at a lower energy level than the reactants. For this and all other exothermic reactions, ΔH is negative.

Tip

Arrows in an energy level diagram should be single-headed – pointing down or up. Never draw double-headed arrows. Activation energy is not shown in an enthalpy level diagram, but is shown in reaction profile diagrams (Section 9.4).

Endothermic changes

Endothermic changes take in energy from the surroundings. They are the opposite of exothermic changes. Melting and vaporisation are endothermic changes of state. Photosynthesis is an endothermic chemical change. During photosynthesis, plants take in energy from the Sun in order to convert carbon dioxide and water to glucose. Figure 8.5 illustrates the use of an endothermic reaction in a cold pack.

An enthalpy level diagram shows that the system has more energy after an endothermic reaction than it had at the start. So, for endothermic reactions, the enthalpy change, ΔH, is positive and the products are at a higher energy level than the reactants (Figure 8.6).

Figure 8.5 Twist a cold pack and it gets cold enough to reduce the pain of a sports injury. When chemicals in the cold pack react, they take in energy and the pack gets cold. This, in turn, cools the sprained or bruised area and helps to reduce painful swelling.

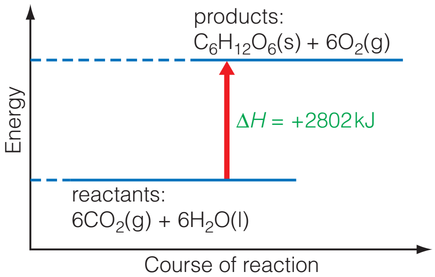


Figure 8.6 An enthalpy level diagram for photosynthesis.

Test yourself

1 Which of the following changes are exothermic and which are endothermic?

- **a)** melting ice
- **b)** burning wood
- **c)** condensing steam
- **d)** metabolising sugar
- **e)** subliming iodine

2 When 1.00 mol of carbon (as graphite) burns completely, 394 kJ of energy is given out.

- **a)** Write an equation for the reaction including state symbols and show the value of the enthalpy change.
- **b)** Draw an enthalpy level diagram for the reaction including the enthalpy change.

3 When 0.200 g of methane, CH_4 (natural gas), burns completely, it gives out 11.0 kJ.

- **a)** Write an equation for the reaction when methane burns completely.
- **b)** Calculate the molar mass of methane.
- **c)** Calculate the energy change when 1.00 mol of methane burns completely.
- **d)** Draw an enthalpy level diagram for the reaction showing the value of the enthalpy change.

Tip

Chemists measure *changes* in enthalpy. Energy level diagrams show the difference in enthalpy between the reactants and the products. It is not possible to put a scale on these diagrams to show the absolute levels of energy in a system.

8.3 Measuring enthalpy changes

The energy given out or taken in during many chemical reactions can be measured and this makes it possible to calculate enthalpy changes.

Enthalpy changes from burning fuels

Figure 8.7 shows the simple apparatus that can be used to measure the energy given out from a liquid fuel like methylated spirit (meths). Meths is ethanol that is made undrinkable by adding some methanol which is toxic.

The results can be used to calculate the energy given out when one mole of the fuel burns. This is the enthalpy of combustion of the fuel.

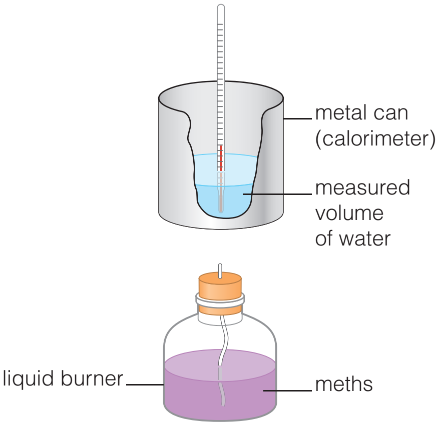


Figure 8.7 Measuring the enthalpy change when meths is burned. Wear eye protection if you try this experiment and remember that liquid fuels are highly flammable.

Key term

The **specific heat capacity** of a material, *c*, is the energy needed to raise the temperature of 1 g of the material by 1 K.

For water $c = 4.18\,\text{J}\,\text{g}^{-1}\,\text{K}^{-1}$.

Tip

Temperatures in thermodynamics are measured on the Kelvin scale. However the size of a temperature change is the same on the Celsius and Kelvin scales. A temperature change of 1 °C is the same as a change of 1 K.

The copper can is acting as a calorimeter. This name means 'calorie–measurer' and is based on the energy unit called the 'calorie'.

Tip

The calorie is the energy need to raise the temperature of 1 g water by 1 °C. 1 calorie = 4.18 J. The food industry often uses the 'large calorie', which is one thousand times larger. 1 Cal = 4.18 kJ.

Typically, a calorimeter is insulated from its surroundings and contains water. The energy from the reaction heats up the water and the rest of the apparatus. An accurate thermometer measures the temperature rise.

The energy transferred to a material can be calculated using this expression:

$$\text{energy transferred/J} = \text{mass/g} \times \text{specific heat capacity/J}\,\text{g}^{-1}\,\text{K}^{-1} \times \text{temperature rise/K}$$

If Q represents the energy transferred, this can be written as:

$$Q = mc\Delta T$$

The **specific heat capacity** of water is $4.18\,\text{J}\,\text{g}^{-1}\,\text{K}^{-1}$. This means that:

4.18 J raises the temperature of 1 g of water by 1 K

$m \times 4.18$ J raises the temperature of a mass *m,* in grams, of water by 1 K

and

$m \times 4.18\,\text{J}\,\text{g}^{-1}\,\text{K}^{-1} \times \Delta T$ raises the temperature of a mass *m,* in grams, of water by ΔT

Example

Table 8.1 shows the results from an experiment to measure the energy given out by burning meths using the apparatus shown in Figure 8.7. Use the results to work out the enthalpy of combustion of meths.

Table 8.1 Results from an experiment to measure the energy given out by burning meths (ethanol).

Mass of burner + meths at start of experiment	= 271.80 g
Mass of burner + meths at end of experiment	= 271.30 g
Volume of water in can	= 250 cm^3
Rise in temperature of water	= 10.0 °C = 10.0 K

Notes on the method

This calculation assumes that *all* the energy given out from the burning meths heats up the water.

The density of water is $1.0\,\text{g}\,\text{cm}^{-3}$. So the mass of $100\,\text{cm}^3$ water is 100 g.

- From the mass of water in the can and its temperature rise, work out the energy transferred.

- From the loss in mass of the liquid burner, find the mass of meths which burned.
- Calculate the energy given out per gram of fuel.
- Multiply by the molar mass of meths (ethanol) to calculate the energy given out per mole of fuel
- Give an answer to an appropriate number of significant figures (see Section A1.4 in Appendix A1).

Answer

From the data in the table:

- mass of water in the can = 250 g
- temperature rise = 10.0 K

Energy transferred to the water in the can

$$= 250\,\text{g} \times 4.18\,\text{J}\,\text{g}^{-1}\,\text{K}^{-1} \times 10.0\,\text{K} = 10\,450\,\text{J}$$

Mass of meths burned = 0.50 g

Energy given out per gram of meths that burned $= 10\,450\,\text{J} \div 0.50\,\text{g}$

$$= 20\,900\,\text{J}\,\text{g}^{-1}$$

Molar mass of meths (ethanol, C_2H_6O) $= 46.0\,\text{g}\,\text{mol}^{-1}$

Energy given out when one mole of ethanol (meths) burns

$$= 20\,900\,\text{J}\,\text{g}^{-1} \times 46.0\,\text{g}\,\text{mol}^{-1}$$

$$= 961\,400\,\text{J}\,\text{mol}^{-1} = 961.4\,\text{kJ}\,\text{mol}^{-1}$$

The enthalpy change of combustion of a fuel is given the symbol $\Delta_c H$. There are many sources of error in this crude method of measuring enthalpy changes and so the data should not be quoted to more than two significant figures.

Therefore, from these results the value for of enthalpy change of this exothermic reaction is given by:

$$\Delta_c H\ [\text{ethanol}] = -960\,\text{kJ}\,\text{mol}^{-1}$$

In summary:

$$C_2H_6O(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -960\,\text{kJ}\,\text{mol}^{-1}$$

Tip

In calculations with several steps it is better not to use your calculator at each stage. The danger is that you introduce 'rounding errors' at every step. You will get a more accurate answer if you work out the answer at the end.

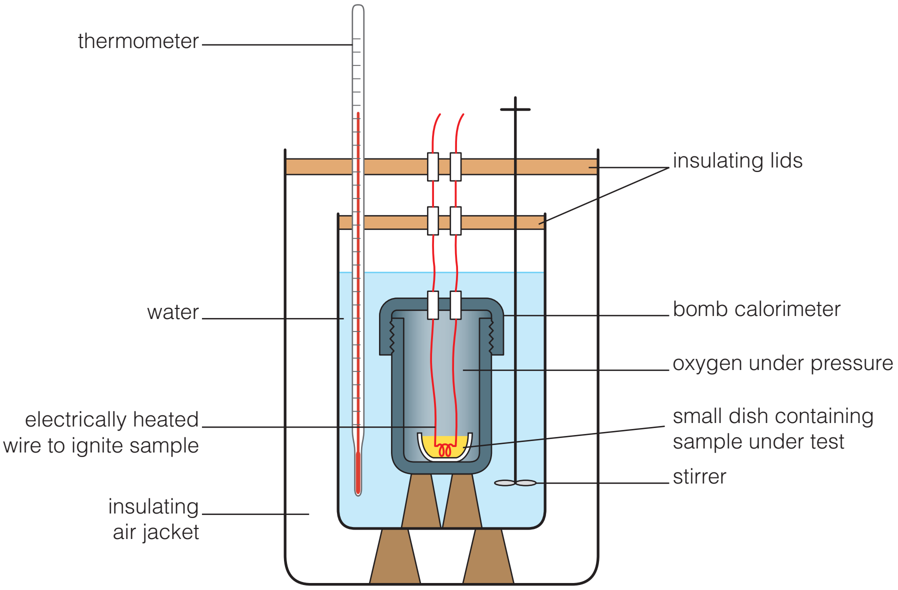
Assumptions and errors in thermochemical experiments

In the experiment in the example, the calculation is based on the assumption that *all* the energy from the flame heats the water. In practice much of the energy heats the metal can and the surrounding air. In addition, the flame is affected by draughts and sometimes the fuel burns incompletely, leaving soot on the bottom of the metal can. So, the assumption is clearly flawed. The result is certainly inaccurate. The major sources of error (loss of energy, flame disturbance and incomplete combustion) all reduce the energy transferred to the water. This leads to a result that is less exothermic than the true value.

Accurate values for energy changes during combustion are obtained using a bomb calorimeter (Figure 8.8). The apparatus is specially designed to ensure that the sample burns completely and that energy losses are avoided. A measured amount of the sample burns in excess oxygen under pressure.

There is enough oxygen to ensure that all carbon in the compound is fully oxidised to carbon dioxide and no carbon monoxide or soot are produced. The energy change is measured at constant volume so a correction is needed to calculate the enthalpy change at constant pressure.

Figure 8.8 A bomb calorimeter.


thermometer
insulating lids
water
bomb calorimeter
oxygen under pressure
electrically heated wire to ignite sample
small dish containing sample under test
stirrer
insulating air jacket

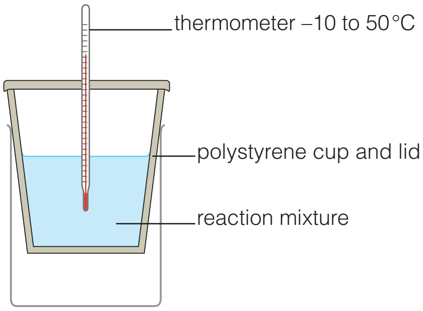

thermometer –10 to 50 °C
polystyrene cup and lid
reaction mixture

Figure 8.9 Measuring the enthalpy change of a reaction in solution.

Enthalpy changes in solution

Enthalpy changes for reactions in solution can be measured using insulated plastic containers such as polystyrene cups as calorimeters (Figure 8.9). Polystyrene is an excellent insulator and it has a negligible specific heat capacity.

If the reaction is exothermic, the energy released cannot escape to the surroundings, so it heats up the solution. If the reaction is endothermic, no energy can enter from the surroundings, so the solution cools. If the solutions are dilute, it is sufficiently accurate to calculate the enthalpy changes by assuming that the solutions have the same density and specific heat capacity as water.

The temperature changes are often quite small and so it is important to use a thermometer that is graduated in tenths of a degree.

Example

When 4.00 g of ammonium nitrate (NH_4NO_3) dissolves in 100 cm^3 of water, the temperature falls by 3.0 °C. Calculate the enthalpy change per mole when NH_4NO_3 dissolves in water under these conditions.

Notes on the method

Calculate the energy change by assuming that the solution has the same specific heat capacity (4.18 J g^{-1} K^{-1}) and density (1.00 g cm^{-3}) as water.

Work out the amount in moles of ammonium nitrate added.

Divide the energy change by the amount to determine the energy change in kJ mol^{-1}.

Answer

Energy taken in from the solution

= mass × specific heat capacity × temperature change

$= 100\,\text{g} \times 4.18\,\text{J g}^{-1}\,\text{K}^{-1} \times 3.0\,\text{K}$

$= 1254\,\text{J}$

$$\text{Amount of NH}_4\text{NO}_3 = \frac{\text{mass of NH}_4\text{NO}_3}{\text{molar mass of NH}_4\text{NO}_3} = \frac{4.00\,\text{g}}{80.0\,\text{g mol}^{-1}}$$

$$= 0.050\,\text{mol}$$

$$\text{Energy taken in per mole of NH}_4\text{NO}_3 = \frac{1254\,\text{J}}{0.050\,\text{mol}} = 25\,080\,\text{J mol}^{-1}$$

$$= 25\,\text{kJ mol}^{-1}\ \text{(2 significant figures)}$$

The reaction is endothermic, so the enthalpy change for the system is positive.

$$\text{NH}_4\text{NO}_3\text{(s)} \xrightarrow{+\text{aq}} \text{NH}_4\text{NO}_3\text{(aq)} \qquad \Delta H = +25\,\text{kJ mol}^{-1}$$

Test yourself

4 Burning butane, C_4H_{10}, from a Camping Gaz® container raised the temperature of 200 g water from 18.0 °C to 28.0 °C. The Gaz® container was weighed before and after, and the loss in mass was 0.29 g. Estimate the molar enthalpy change of combustion of butane.

5 On adding $25\,\text{cm}^3$ of $1.0\,\text{mol dm}^{-3}$ nitric acid to $25\,\text{cm}^3$ of $1.0\,\text{mol dm}^{-3}$ potassium hydroxide in a plastic cup, the temperature rise is 6.5 °C.

- **a)** Write an equation for the reaction.
- **b)** Calculate the enthalpy change for the neutralisation reaction per mole of nitric acid.

6 On adding excess powdered zinc to $25\,\text{cm}^3$ of $0.20\,\text{mol dm}^{-3}$ copper(II) sulfate solution, the temperature rises by 9.5 °C.

- **a)** Write an equation for the reaction.
- **b)** Calculate the enthalpy change of the reaction for the molar amounts in the equation.

8.4 Standard enthalpy changes

The values of enthalpy changes vary with changes in temperature, pressure or concentration. This means that the conditions have to be carefully specified for the **standard enthalpy changes** listed in data tables.

The standard conditions are:

- a pressure of 100 kPa (this is the approximate pressure of the atmosphere at sea level)
- a stated temperature that is usually 298 K (25 °C)
- substances in their standard (most stable) state at 100 kPa pressure and the stated temperature
- solutions with a concentration of $1\,\text{mol dm}^{-3}$.

Key term

The **standard enthalpy change of a reaction**, $\Delta_r H^{\ominus}$, is the energy transferred when the molar quantities of reactants as stated in the equation react under standard conditions.

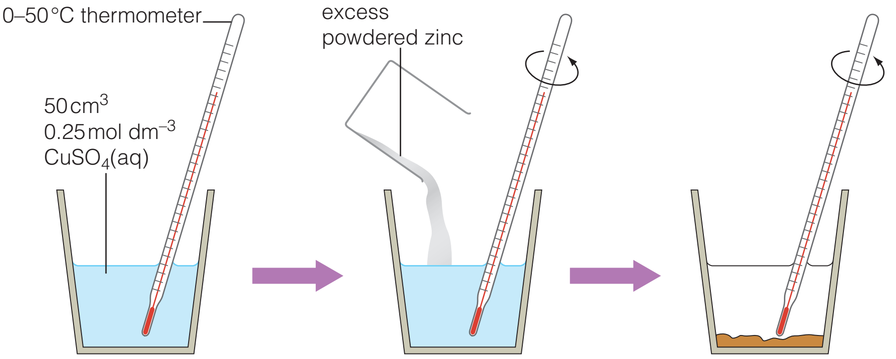
Activity

Measuring and evaluating the enthalpy change for the reaction of zinc with copper(II) sulfate solution

Two students decided to measure the enthalpy change for the reaction between zinc and copper(II) sulfate solution.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

The method which they used is shown in Figure 8.10 and their results are shown in Table 8.2. After adding the zinc, it took a little while for the temperature to reach a peak and then the mixture began to cool.



Measure the temperature every 30 s for 2.5 minutes.

At 3.0 minutes add excess powdered zinc and stir.

Continue stirring and record the temperature every 30 s for a further 6 minutes.

Figure 8.10 Measuring the enthalpy change for the reaction of zinc with copper(II) sulfate solution.

Table 8.2

Time/min	Temperature /°C	Time/min	Temperature /°C	Time/min	Temperature /°C
0	24.1	3.5	34.2	6.5	33.7
0.5	24.0	4.0	34.8	7.0	33.6
1.0	24.1	4.5	35.0	7.5	33.5
1.5	24.1	5.0	34.6	8.0	33.4
2.0	24.2	5.5	34.2	8.5	33.2
2.5	24.1	6.0	33.9	9.0	33.1
3.0	–				

1. Plot a graph of temperature (vertically) against time (horizontally) using the results in Table 8.2.
2. Extrapolate the graph backwards from 9 minutes to 3 minutes, as in Figure 8.11. This gives an estimate of the maximum temperature if all the zinc had reacted at once and there was no loss of energy to the surroundings.
   a) What is the estimated maximum temperature at 3 minutes?
   b) What is the temperature rise, ΔT, for the reaction?
3. Calculate the energy given out during the reaction using the equation:

energy transferred = mass × specific heat capacity × temperature change

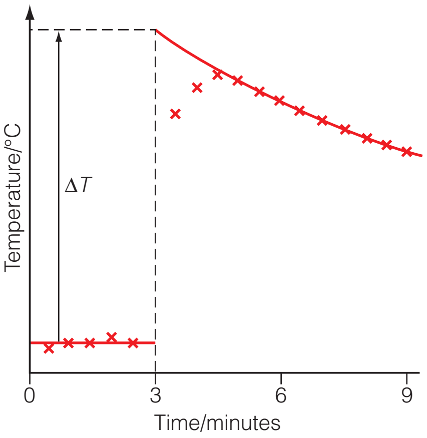


Figure 8.11 Estimating the maximum temperature of the mixture when zinc reacts with copper(II) sulfate solution.

Assume that:

- all the energy is transferred to the solution in the polystyrene cup
- the density of the solution is 1.0 g cm^{-3}
- the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}.

4 How many moles of each chemical reacted?

a) $CuSO_4$ **b)** Zn

5 What is the enthalpy change of the reaction, $\Delta_r H$, for the amounts of Zn and $CuSO_4$ in the equation? (State the value of $\Delta_r H$ in kJ mol^{-1} with the correct sign.)

6 With the help of Practical skills sheet 5, which you can access via the QR code for Chapter 8 on page 313, copy and complete Table 8.3 for the various measurements in the experiment.

Table 8.3 The values, uncertainties and percentage uncertainties of measurements in the experiment.

Measurement	Value	Uncertainty	Percentage uncertainty
Concentration of copper(II) sulfate solution			
Volume of copper(II) sulfate solution measured from a 100 cm^3 measuring cylinder			
Temperature rise, ΔT, estimated from the difference in two readings taken with a 0–50 °C thermometer			

7 What is the total percentage uncertainty in the experiment?

8 What is the total uncertainty in the value you have calculated for the enthalpy change?

9 Write a value for the enthalpy change showing the uncertainty using the symbol ±.

10 What are the main sources of error in the measurements and procedure for the experiment?

11 Look critically at the procedures in the experiment and suggest improvements to minimise errors and increase the repeatability of the result.

Any enthalpy change measured under standard conditions is described as a standard enthalpy change and given the symbol $\Delta H^{\ominus}_{298}$ or simply $\Delta H^{\ominus}$, pronounced 'delta *H* standard' (Figure 8.12).

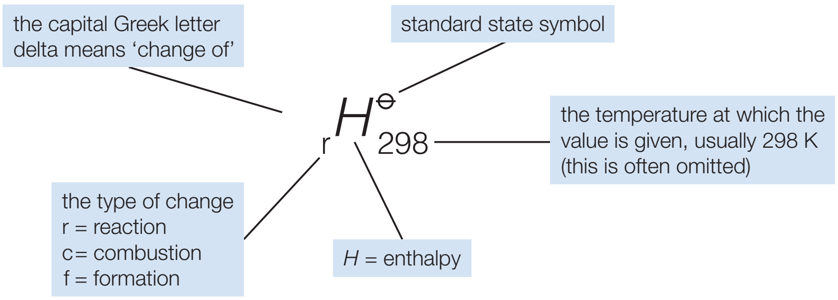

the capital Greek letter delta means 'change of'
standard state symbol
$_rH^{\ominus}_{298}$
the temperature at which the value is given, usually 298 K (this is often omitted)
the type of change
r = reaction
c= combustion
f = formation
H = enthalpy

Figure 8.12 The symbol for a standard enthalpy change.

In thermochemistry, it is important to specify the states of the substances and, therefore, to include state symbols in equations. So, $\Delta H^{\ominus}$ for the reaction:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

must relate to hydrogen gas, oxygen gas and liquid water (not steam). The states of elements and compounds must also be the most stable at the given temperature (often 298 K) and 100 kPa. Thus, $\Delta H^{\ominus}$ measurements involving carbon refer to graphite, which is energetically more stable than diamond.

Standard enthalpy changes of combustion

Key term

The **standard enthalpy change of combustion** of a substance, $\Delta_c H^{\ominus}$ is the enthalpy change when one mole of the substance burns completely in oxygen under standard conditions.

The **standard enthalpy change of combustion** of an element or compound, $\Delta_c H^{\ominus}$, is the enthalpy change when one mole of the substance burns completely in oxygen under standard conditions. The substance and the products of burning must be in their stable (standard) states. For a carbon compound, complete combustion means that all the carbon burns to carbon dioxide and there is no soot or carbon monoxide. If the substance contains hydrogen, the water formed must end up as liquid and not as a gas.

Values of enthalpies of combustion are much easier to measure than many other enthalpy changes. They can be calculated from measurements taken with a bomb calorimeter (Section 8.3).

Chemists use two ways to summarise standard enthalpy changes of combustion. One way is to write the equation with the enthalpy change alongside it. So, for the standard enthalpy change of combustion of carbon, they write:

Tip

Remember that all combustion reactions are exothermic, so $\Delta_c H^{\ominus}$ values are always negative.

$$C_{(graphite)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta_c H^{\ominus} = -394\,\text{kJ}\,\text{mol}^{-1}$$

The other way is to use a shorthand form. For the standard enthalpy change of combustion of methane, this is written as:

$$\Delta_c H^{\ominus}[CH_4(g)] = -890\,\text{kJ}\,\text{mol}^{-1}$$

Standard enthalpy changes of formation

Key term

The **standard enthalpy change of formation** of a compound, $\Delta_f H^{\ominus}$, is the enthalpy change when one mole of the compound forms from its elements under standard conditions with the elements and the compound in their standard (stable) states.

The **standard enthalpy change of formation** of a compound, $\Delta H_f^{\ominus}$, is the enthalpy change when one mole of the compound forms from its elements. The elements and the compound formed must be in their stable standard states. The more stable state of an element is chosen where there are allotropes (different forms in the same state) such as graphite and diamond.

As with standard enthalpies of combustion, there are two ways of representing standard enthalpy changes of formation.

One way is to write the equation with the enthalpy change alongside it. For the standard enthalpy change of formation of water this is:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta_f H^{\ominus} = -286\,\text{kJ}\,\text{mol}^{-1}$$

The other way is to use shorthand. For the standard enthalpy change of formation of ethanol this is:

$$\Delta_f H^{\ominus}[C_2H_5OH(l)] = -277\,\text{kJ}\,\text{mol}^{-1}$$

Like all thermochemical quantities, the precise definition of the standard enthalpy change of formation is important. Books of data tabulate values for standard enthalpies of formation. These tables are very useful because they make it possible to calculate the enthalpy changes for many reactions (Section 8.5).

Unfortunately, it is difficult to measure some enthalpy changes of formation directly. For example, it is impossible to convert carbon, hydrogen and oxygen straight to ethanol under any conditions. Because of this, chemists have had to find an indirect method of measuring the standard enthalpy change of formation of ethanol and other compounds (Section 8.5).

One important consequence of the definition of standard enthalpy changes of formation is that, for an element, $\Delta_f H^\ominus = 0\,\mathrm{kJ\,mol^{-1}}$ because there is no change, and therefore no enthalpy change, when an element forms from itself. In other words, the standard enthalpy change of formation of an element is zero. So:

$\Delta_f H^\ominus[\mathrm{Cu(s)}] = 0$ and $\Delta_f H^\ominus[\mathrm{O_2(g)}] = 0$

Standard enthalpy changes of neutralisation

Many chemical reactions happen in solution. Chemists define standard enthalpy changes for changes in solution including the **standard enthalpy change of neutralisation**. This is usually defined as the enthalpy change per mole of water formed.

Key term

The **standard enthalpy change of neutralisation** is the enthalpy change when the acid and alkali in the equation for the reaction neutralise each other under standard conditions to form one mole of water.

Example

When 50.0 $\mathrm{cm^3}$ of 2.00 $\mathrm{mol\,dm^{-3}}$ hydrochloric acid is mixed with 50.0 $\mathrm{cm^3}$ of 2.00 $\mathrm{mol\,dm^{-3}}$ sodium hydroxide in a calorimeter at 25 °C and 100 kPa, the temperature rises by 13.7 °C. Calculate the enthalpy change for the neutralisation reaction.

Notes on the method

Write the equation for the reaction.

Assume that the dilute solution has the same specific heat capacity ($4.18\,\mathrm{J\,g^{-1}\,K^{-1}}$) and density ($1\,\mathrm{g\,cm^{-3}}$) as water.

Calculate the energy change in the calorimeter, taking care to use the total mass of water.

Next calculate the amount of hydrochloric acid that reacted.

Divide the energy change by the amount in moles to determine the enthalpy change per mole of water formed.

Give the answer to an appropriate number of significant figures.

Answer

The equation for the reaction is:

$$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

This shows that 1 mol acid reacts to form 1 mol water.

Energy given out and used to heat 100 $\mathrm{cm^3}$ of solution

$$= 100\,\mathrm{g} \times 4.18\,\mathrm{J\,g^{-1}\,K^{-1}} \times 13.7\,\mathrm{K} = 5727\,\mathrm{J}$$

Amount of HCl used = amount of NaOH used

$$= \frac{50.0}{1000}\,\mathrm{dm^3} \times 2.00\,\mathrm{mol\,dm^{-3}} = 0.100\,\mathrm{mol}$$

Energy given out per mole of acid $= \dfrac{5727\,\mathrm{J}}{0.100\,\mathrm{mol}} = 57\,270\,\mathrm{J\,mol^{-1}}$

For this neutralisation reaction $\Delta H = -57.3\,\mathrm{kJ\,mol^{-1}}$

Now, as the concentrations of the two solutions were effectively 1.0 mol dm^{-3} immediately after mixing, the temperature was 25 °C and the pressure 100 kPa, the value of the enthalpy change of neutralisation has been obtained under standard conditions.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

$$\Delta_n H^{\ominus} = -57.3\ kJ\ mol^{-1}$$

This is the standard enthalpy change of neutralisation for this reaction.

Test yourself

7 By writing a balanced equation, show that the standard enthalpy change of formation of carbon dioxide is the same as the standard enthalpy change of combustion of carbon (graphite).

8 Write equations for the reactions for which the enthalpy change is the standard enthalpy change of formation of:

- **a)** aluminium oxide, $Al_2O_3(s)$
- **b)** hydrogen chloride, $HCl(g)$
- **c)** propane, $C_3H_8(g)$.

9 The temperature change on mixing 25 cm^3 of 1.0 mol dm^{-3} hydrochloric acid with 25 cm^3 of 1.0 mol dm^{-3} potassium hydroxide is 6.5 °C. What is the temperature on mixing 50 cm^3 each of the same two solutions?

8.5 Hess's Law and the indirect determination of enthalpy changes

Key term

Hess's Law states that the enthalpy change in converting reactants to products is the same regardless of the route taken, provided the initial and final conditions are the same.

The enthalpy change of a reaction is the same whether the reaction happens in one step or in a series of steps. As long as the reactants and products are the same, the overall enthalpy change is the same whether the reactants are converted to products directly or through two or more intermediates. This is **Hess's Law**. In Figure 8.13 the enthalpy change for Route 1 and the overall enthalpy change for Route 2 are the same.

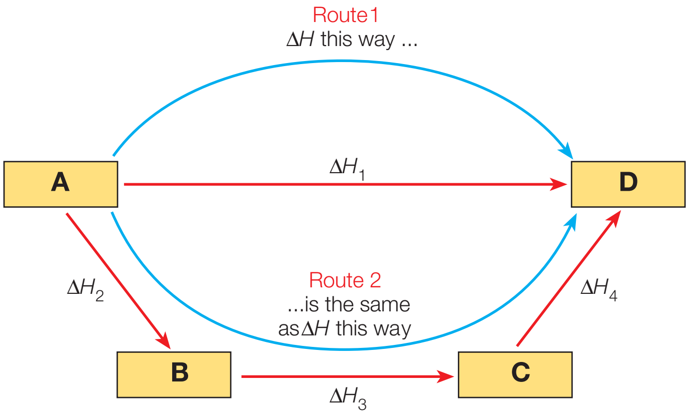


Figure 8.13 A diagram to illustrate Hess's Law: $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$.

Hess's Law is a chemical version of the law of conservation of energy. Suppose the enthalpy change for Route 1 in Figure 8.13 were more exothermic than the total enthalpy change for Route 2. It would then be possible to go round the cycle in Figure 8.13 from A to D direct and back to A via C and B, ending up with the same starting chemical but with a net release of energy. This would contravene the law of conservation of energy.

Hess's Law is also an example of a mathematical model. This is shown by the precise quantitative relationship between ΔH_1, ΔH_2, ΔH_3 and ΔH_4 in Figure 8.13. Using Hess's Law it is possible to bring together data and calculate enthalpy changes which cannot be measured directly by experiment. So, Hess's Law can be used to calculate:

- standard enthalpy changes of formation from standard enthalpy changes of combustion and
- standard enthalpy changes of reaction from standard enthalpy changes of formation.

Tip

The standard enthalpy changes for other reactions can be calculated using standard enthalpy changes of combustion. However, it is the determination of standard enthalpy changes of formation that is particularly important because these are the values that are used in many thermochemical calculations.

Enthalpy changes of formation from enthalpy change of combustion

Figure 8.14 shows the form of the energy cycle which we can use to calculate enthalpy changes of formation from enthalpy changes of combustion.

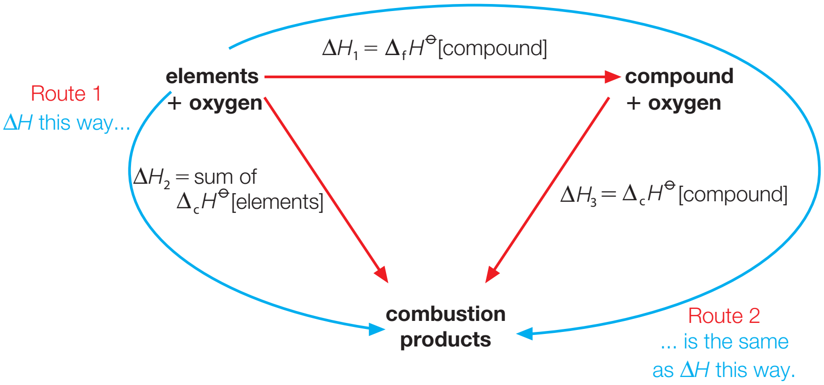

$\Delta H_1 = \Delta_f H^\ominus$[compound]
elements + oxygen
compound + oxygen
Route 1
ΔH this way...
ΔH_2 = sum of $\Delta_c H^\ominus$[elements]
$\Delta H_3 = \Delta_c H^\ominus$[compound]
combustion products
Route 2
... is the same as ΔH this way.

Figure 8.14 An energy cycle for calculating standard enthalpy changes of formation from standard enthalpy changes of combustion: $\Delta H_2 = \Delta H_1 + \Delta H_3$.

Example

Calculate the standard enthalpy change of formation of propane, C_3H_8, at 298 K given the following standard enthalpy changes of combustion.

propane, $\Delta_c H^\ominus[C_3H_8(g)] = -2219\ \text{kJ mol}^{-1}$

carbon, $\Delta_c H^\ominus[C_{(graphite)}] = -394\ \text{kJ mol}^{-1}$

hydrogen $\Delta_c H^\ominus\ [H_2(g)] = -286\ \text{kJ mol}^{-1}$

Notes on the method

Draw up an energy cycle using the model in Figure 8.15. Use Hess's Law to produce an equation linking the relevant enthalpy changes.

Pay careful attention to the signs.

Put the value and sign for a quantity in brackets when adding or subtracting enthalpy values.

Answer

An energy cycle linking the formation of propane with its combustion and the combustion of its constituent elements is shown in Figure 8.15. Sometimes, energy cycles like the one in Figure 8.15 are called Hess cycles.

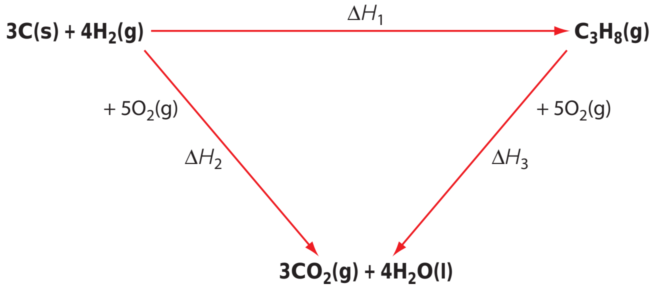


Figure 8.15 An energy cycle for the combustion of propane and its constituent elements.

According to Hess's Law:

$$\Delta H_2 = \Delta H_1 + \Delta H_3$$

$$\Delta H_2 = 3 \times \Delta_c H^\ominus[C_{(graphite)}] + 4 \times \Delta_c H^\ominus[H_2(g)]$$

$$= 3 \times (-394\ \text{kJ mol}^{-1}) + 4 \times (-286\ \text{kJ mol}^{-1}) = -2326\ \text{kJ mol}^{-1}$$

$$\Delta H_1 = \Delta_f H^\ominus[C_3H_8(g)]$$

$$\Delta H_3 = \Delta_c H^\ominus[C_3H_8(g)] = -2219\ \text{kJ mol}^{-1}$$

Hence:

$$(-2323\ \text{kJ mol}^{-1}) = \Delta_f H^\ominus[C_3H_8(g)] + (-2220\ \text{kJ mol}^{-1})$$

$$\Delta_f H^\ominus[C_3H_8(g)] = (-2326\ \text{kJ mol}^{-1}) - (-2219\ \text{kJ mol}^{-1})$$

$$= -2326\ \text{kJ mol}^{-1} + 2219\ \text{kJ mol}^{-1}$$

$$= -107\ \text{kJ mol}^{-1}$$

Test yourself

10 Use the values of standard enthalpy changes of combustion below to calculate the standard enthalpy change of formation of methanol, CH_3OH.

$\Delta_c H^\ominus[CH_3OH(l)] = -726\,kJ\,mol^{-1}$

$\Delta_c H^\ominus[C_{(graphite)}] = -394\,kJ\,mol^{-1}$

$\Delta_c H^\ominus[H_2(g)] = -286\,kJ\,mol^{-1}$

11 Why is it useful to have standard enthalpy changes of combustion which can be used to calculate standard enthalpy changes of formation?

Enthalpy changes of reaction from enthalpy changes of formation

Data books contain tables of standard enthalpies of formation for both inorganic and organic compounds. The great value of this data is that it allows chemists to calculate the standard enthalpy change for any reaction involving the substances listed in the tables.

The standard enthalpy change of a reaction is the enthalpy change when the amounts shown in the chemical equation react. Like other standard quantities in thermochemistry, the standard enthalpy change of reaction is defined at 100 kPa pressure with the reactants and products in their normal stable states at a particular temperature, usually 298 K. The concentration of any solution is 1.0 mol dm^{-3}.

Thanks to Hess's Law it is easy to calculate the standard enthalpy change of a reaction from tabulated values of standard enthalpy changes of formation (Figure 8.16).

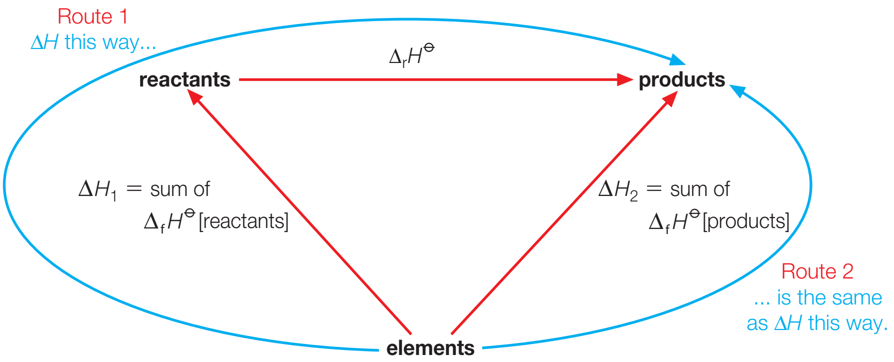

Route 1
ΔH this way...
$\Delta_r H^\ominus$
reactants
products
ΔH_1 = sum of $\Delta_f H^\ominus$[reactants]
ΔH_2 = sum of $\Delta_f H^\ominus$[products]
Route 2
... is the same as ΔH this way.
elements

Figure 8.16 An energy cycle for calculating standard enthalpies of reaction from standard enthalpies of formation.

According to Hess's Law:

$$\Delta H_1 + \Delta_r H^\ominus = \Delta H_2$$

Rearranging gives:

$$\Delta_r H^\ominus = \Delta H_2 - \Delta H_1$$

So:

$$\Delta_r H^\ominus = \text{sum of } \Delta_f H^\ominus[\text{products}] - \text{sum of } \Delta_f H^\ominus[\text{reactants}]$$

Tip

Take care! Enthalpy changes for reactions can also be calculated from enthalpy changes of combustion. The relationship is then:

$$\Delta_r H^\ominus = \text{sum of } \Delta_c H^\ominus[\text{reactants}] - \text{sum of } \Delta_c H^\ominus[\text{products}]$$

So do not learn these formulae parrot fashion. Check with the Hess cycle each time.

Example

Calculate the standard enthalpy change for the reduction of iron(III) oxide by carbon monoxide.

$\Delta_f H^{\ominus}[Fe_2O_3] = -824\,kJ\,mol^{-1}$

$\Delta_f H^{\ominus}[CO] = -110\,kJ\,mol^{-1}$

$\Delta_f H^{\ominus}[CO_2] = -394\,kJ\,mol^{-1}$

Notes on the method

Write the balanced equation for the reaction and then draw an energy cycle (Hess cycle) using the model in Figure 8.17.

Remember that, by definition, $\Delta_f H^{\ominus}[\text{element}] = 0\,kJ\,mol^{-1}$.

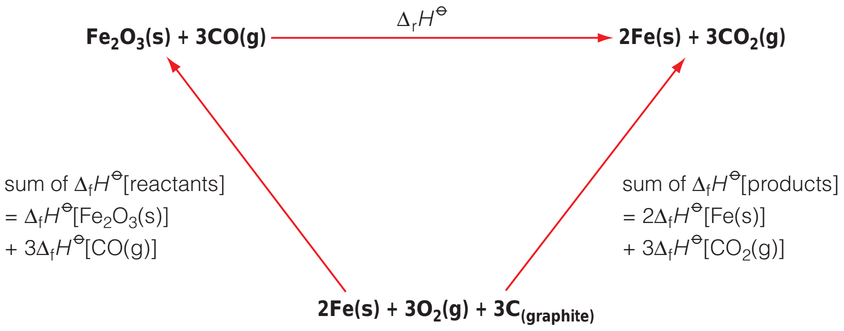
Pay careful attention to the signs. Put the value and sign for a quantity in brackets when adding or subtracting enthalpy values.

Tip

Reversing the direction of a reaction in an energy cycle reverses the sign of ΔH.

Answer

$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$



$\Delta_r H^{\ominus}$
$Fe_2O_3(s) + 3CO(g)$
$2Fe(s) + 3CO_2(g)$
sum of $\Delta_f H^{\ominus}$[reactants]
$= \Delta_f H^{\ominus}[Fe_2O_3(s)]$
$+ 3\Delta_f H^{\ominus}[CO(g)]$
sum of $\Delta_f H^{\ominus}$[products]
$= 2\Delta_f H^{\ominus}[Fe(s)]$
$+ 3\Delta_f H^{\ominus}[CO_2(g)]$
$2Fe(s) + 3O_2(g) + 3C_{(graphite)}$

Figure 8.17 An energy cycle (Hess cycle) for calculating the enthalpy change of reaction between iron(III) oxide and carbon monoxide.

Applying Hess's Law to Figure 8.17:

$\Delta_r H^{\ominus} = \text{sum of } \Delta_f H^{\ominus}[\text{products}] - \text{sum of } \Delta_f H^{\ominus}[\text{reactants}]$

$\Delta_r H^{\ominus} = \{2 \times \Delta_f H^{\ominus}[Fe] + 3 \times \Delta_f H^{\ominus}[CO_2]\} - \{\Delta_f H^{\ominus}[Fe_2O_3] + 3 \times \Delta_f H^{\ominus}[CO]\}$

$= \{0 + (3 \times -394\,kJ\,mol^{-1})\} - \{(-824\,kJ\,mol^{-1}) + (3 \times -110\,kJ\,mol^{-1})\}$

$= -1182\,kJ\,mol^{-1} + 824\,kJ\,mol^{-1} + 330\,kJ\,mol^{-1}$

$\Delta_r H^{\ominus} = -28\,kJ\,mol^{-1}$

Test yourself

12 The standard enthalpy change of formation of sucrose (sugar), $C_{12}H_{22}O_{11}$, is $-2226\,kJ\,mol^{-1}$. Write the balanced equation for which the standard enthalpy change of reaction is $-2226\,kJ\,mol^{-1}$.

13 When calculating standard enthalpy changes for reactions involving water at 298 K, why is it important to specify that the H_2O is present as water and not as steam?

14 Calculate the standard enthalpy change for the reaction of one mole of hydrazine, $N_2H_4(l)$ with oxygen, O_2, to form nitrogen, N_2, and water, H_2O.

$$\Delta_f H^{\ominus}[N_2H_4(l)] = +51\,\text{kJ mol}^{-1}$$

$$\Delta_f H^{\ominus}[H_2O(l)] = -286\,\text{kJ mol}^{-1}$$

Core practical 8

Applying Hess's Law to find an enthalpy change that cannot be measured directly

Two students decided to determine the enthalpy change for the hydration of magnesium sulfate to give crystals of the hydrated salt.

$$MgSO_4(s) + 7H_2O(l) \longrightarrow MgSO_4.7H_2O(s)$$

It is not possible to measure this enthalpy change directly because of the difficulty of controlling the temperature and measuring the temperatures of solids. The students were given the Hess's Law cycle in Figure 8.18 which shows that it is possible to determine the required enthalpy change at room temperature.

$$\begin{tikzcd}
\mathbf{MgSO_4(s) + 7H_2O(l)} \arrow[rr, "\Delta H_1"] \arrow[dr, "+93H_2O(l)"', "\Delta H_2"] & & \mathbf{MgSO_4.7H_2O(s)} \arrow[dl, "+93H_2O(l)", "\Delta H_3"'] \\
& \mathbf{MgSO_4(aq, 100H_2O)} &
\end{tikzcd}$$

Figure 8.18 An energy cycle (Hess cycle) for calculating the enthalpy change of the reaction.

Figure 8.19 shows the procedure that the students used for determining ΔH_2. They used a 0–50 °C thermometer with 0.2 °C graduations. They then used exactly the same procedure to determine ΔH_3 using hydrated magnesium sulfate in place of the anhydrous salt and a little less water.

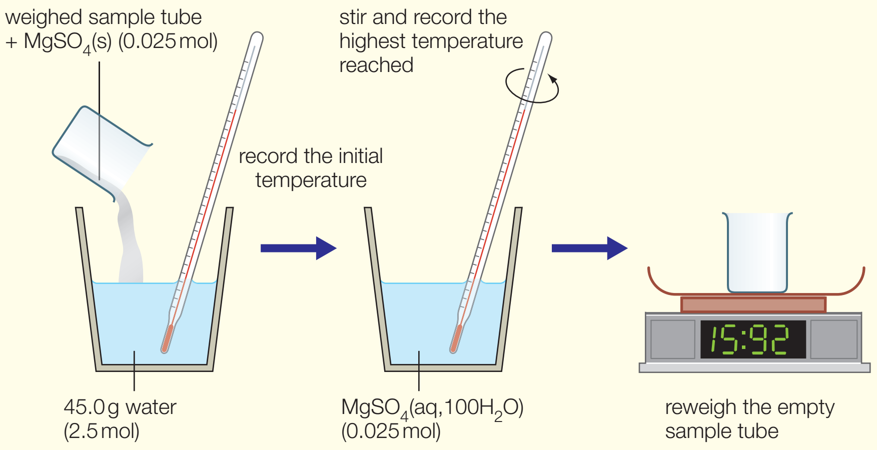

weighed sample tube
+ $MgSO_4(s)$ (0.025 mol)
stir and record the highest temperature reached
record the initial temperature
15:92
45.0 g water
(2.5 mol)
$MgSO_4(aq, 100H_2O)$
(0.025 mol)
reweigh the empty sample tube

Figure 8.19 Outline of a procedure for measuring the enthalpy change when anhydrous magnesium sulfate reacts with and dissolves in a measured amount of water.

Results

Table 8.4 Results for the anhydrous and for the hydrated salt.

Results for anhydrous salt	
Mass of sample tube + $MgSO_4(s)$	12.91 g
Mass of empty sample tube	15.92 g
Mass of polystyrene cup + water	47.10 g
Mass of empty cup	2.10 g
Mass of water	45.00 g
Temperature of the solution after reaction	35.4 °C
Starting temperature of the water	24.1 °C

Results for hydrated salt	
Mass of sample tube + $MgSO_4.7H_2O(s)$	19.58 g
Mass of empty sample tube	13.42 g
Mass of polystyrene cup + water	44.21 g
Mass of empty cup	2.36 g
Mass of water	41.85 g
Temperature of the solution after reaction	23.4 °C
Starting temperature of the acid	24.8 °C

1 Show that the ratio of the amount of water, in moles, to the amount of $MgSO_4$ in Figure 8.19 is 100 : 1.

2 Explain why the hydrated salt was added to less water (as shown in Table 8.4) so that in both reactions the mixture at the end was the same and equivalent to $MgSO_4(aq, 100H_2O)$.

3 **a)** For the anhydrous salt, work out the mass of salt added and the temperature change.

b) Calculate the energy change on adding the anhydrous salt to excess water and hence determine ΔH_2.

4 **a)** For the hydrated salt, work out the mass of salt added and the temperature change.

b) Calculate the energy change on adding the hydrated salt to excess water and hence determine ΔH_3.

5 Write an expression connecting ΔH_1, ΔH_2 and ΔH_3.

6 Calculate ΔH_1 giving your answer to the number of significant figures justified by the data. Account for your choice of number of significant figures.

7 Evaluate the results of the experiment by calculating the standard enthalpy change for the hydration reaction using standard enthalpy changes of formation.

$$\Delta_f H^\ominus[MgSO_4(s)] = -1285\,\text{kJ mol}^{-1}$$

$$\Delta_f H^\ominus[H_2O(l)] = -286\,\text{kJ mol}^{-1}$$

$$\Delta_f H^\ominus[MgSO_4.7H_2O(s)] = -3389\,\text{kJ mol}^{-1}$$

Compare and comment on the two values.

8 The students measured the masses with a balance reading to two decimal places. Would they have reduced the overall error in their results by using a balance reading to three decimal places?

9 Suggest two ways of modifying the procedure shown in Figure 8.19 that would have improved the accuracy of the temperature changes measured by the students.

Tip

Refer to Practical skills sheets 5 and 10, which you can access via the QR code for Chapter 8 on page 313:

5 Identifying errors and estimating uncertainties

10 Measuring enthalpy changes.

8.6 Enthalpy changes and the direction of change

Strike a match and it catches fire and burns. Put a spark to petrol and it burns furiously. These are two exothermic reactions which, once started, tend to 'go'. They are examples of the many exothermic reactions which just keep going once they have started. In general, chemists expect that a reaction will go if it is exothermic.

What this means is that reactions which give out energy to their surroundings are the ones which happen. This ties in with the common experience that change happens in the direction in which energy is spread around and dissipated in the surroundings. So the sign of ΔH is a guide to the likely direction of change, but it is not a totally reliable guide for three main reasons.

- The direction of change may depend on the conditions of temperature and pressure. One example is the condensation of a vapour such as steam. Steam condenses to water below 100 °C and energy is given out. This is an exothermic change.

  $$H_2O(g) \rightarrow H_2O(l) \qquad \Delta H = -44\,\text{kJ mol}^{-1}$$

  At temperatures above 100 °C, the change goes in the opposite direction and this process is endothermic.
- There are some examples of endothermic reactions which occur readily under normal conditions. So some reactions for which ΔH is positive can happen. One example of this is the reaction of citric acid solution with sodium hydrogencarbonate. The mixture fizzes vigorously and cools rapidly. This suggests that there are other factors that determine the direction of change.
- Some exothermic reactions never occur because the rate of reaction is so slow and the mixture of reactants is effectively inert. For example, the change from diamond to graphite is exothermic, but diamonds do not suddenly turn into black flakes.

8.7 Enthalpy changes and bonding

During reactions, the bonds in reactants break and then new bonds form in the products. For example, when hydrogen reacts with oxygen:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Bonds in the H_2 and O_2 molecules break to form H and O atoms (Figure 8.20). New bonds then form between the H and O atoms to produce water, H_2O.

Tip

Bond *breaking* is endothermic.

Bond *making* is exothermic.

Energy is needed to break the bonds between atoms. So, energy must be released when the reverse occurs and a bond forms.

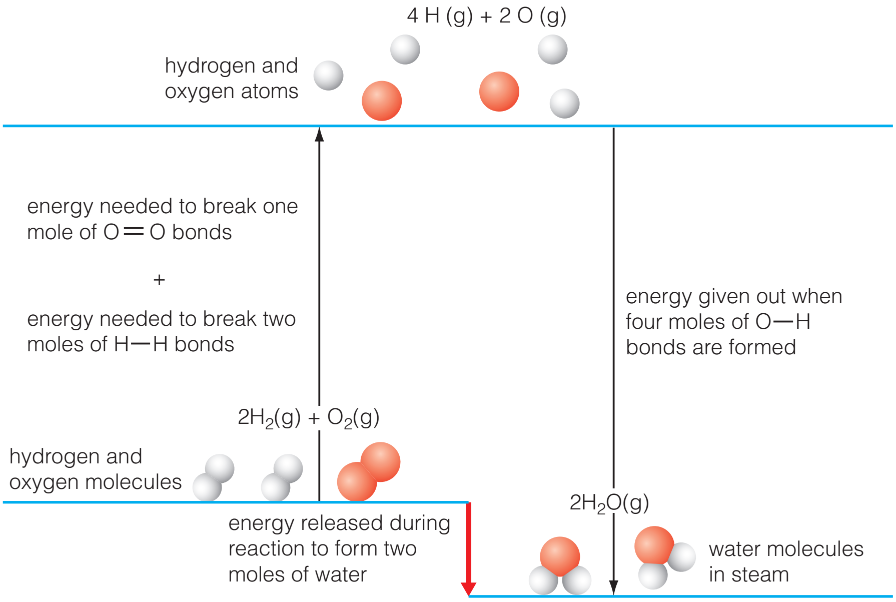

4 H (g) + 2 O (g)
hydrogen and oxygen atoms
energy needed to break one mole of O═O bonds
+
energy needed to break two moles of H—H bonds
energy given out when four moles of O—H bonds are formed
2H$_2$(g) + O$_2$(g)
hydrogen and oxygen molecules
energy released during reaction to form two moles of water
2H$_2$O(g)
water molecules in steam

Figure 8.20 An energy level diagram for the reaction between hydrogen and oxygen.

Chemical reactions involve bond breaking followed by bond making. This means that the enthalpy change of a reaction is the energy difference between bond-breaking and bond-making processes.

When hydrogen and oxygen react, more energy is released in making four new O–H bonds in the two H_2O molecules than in breaking the bonds in two H_2 molecules and one O_2 molecule, so the overall reaction is exothermic (Figure 8.20).

A definite quantity of energy known as the **bond enthalpy** (or bond energy) can be associated with each type of bond. This energy is absorbed when the bond is broken and given out when the bond is formed. In measuring and using bond enthalpies, chemists distinguish between the terms bond enthalpy and mean (average) bond enthalpy.

Bond enthalpies are precise values for specific bonds in compounds (for example the C–Cl bond in CH_3Cl).

Mean bond enthalpies are average values for one kind of bond in different compounds (for example an average value for the C–Cl bond in all compounds). **Mean bond enthalpies** take into account the fact that:

- the bond enthalpy for a specific covalent bond varies slightly from one compound to another (for example the O–H bond has a slightly different bond enthalpy in H_2O and C_2H_5OH)
- successive bond enthalpies are not the same in compounds such as water and methane. (The energy needed to break the first O–H bond in H–O–H(g) is 498 kJ mol^{-1}, but the energy needed to break the second O–H bond in OH(g) is 428 kJ mol^{-1}.)

Key terms

The **bond enthalpy** of a particular bond is the energy required to break one mole of the bonds in a substance in the gaseous state.

The **mean bond enthalpy** of the X–Y bond is the mean value of the bond enthalpy values for the X–Y bond averaged across a wide range of compounds.

Tip

The symbol for bond enthalpy is *E*, so the C–H bond enthalpy is written as *E*(C–H) = 413 kJ mol^{-1}. Values for mean bond enthalpies are given in the data sheet for Chapter 8, which you can access via the QR code for this chapter on page 313.

Using bond enthalpies

The most important use of mean bond enthalpies is in estimating the enthalpy changes in chemical reactions involving molecular substances with covalent bonds. These estimates are particularly helpful when experimental measurements cannot be made, as in the following worked example.

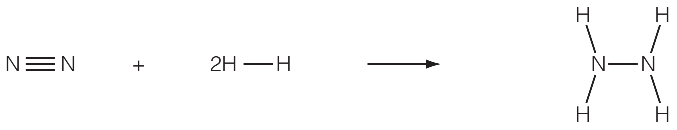
Example

Use mean bond enthalpies to estimate the enthalpy of formation of hydrazine, N_2H_4.

Note on the method

Write the equation for the reaction showing all the atoms and bonds in the molecules. This makes it easier to count the number of bonds broken and formed.

Answer



Bonds broken (endothermic)	Total energy change/ kJ mol^{-1}	Bonds formed	Total energy change/ kJ mol^{-1}
1 × N≡N	+945	1 × N–N	−158
2 × H–H	+(2 × 436)	4 × N–H	−(4 × 391)

$$\begin{aligned}\Delta_r H &= +945\,\mathrm{kJ\,mol^{-1}} + (2 \times 436\,\mathrm{kJ\,mol^{-1}}) \\ &\quad - 158\,\mathrm{kJ\,mol^{-1}} - (4 \times 391\,\mathrm{kJ\,mol^{-1}}) \\ &= +1817\,\mathrm{kJ\,mol^{-1}} - 1722\,\mathrm{kJ\,mol^{-1}} = +95\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

For many reactions, the values of ΔH estimated from mean bond enthalpies agree closely with experimental values. However, there are limitations to the use of bond energy data in this way, and significant differences between the values of ΔH estimated from bond enthalpies and those obtained by experiment do occur. These differences usually arise:

- either from variations in the strength of one kind of bond in different molecules (and mean bond enthalpies should not be used)
- or when one of the reactants or products is not in the gaseous state as bond enthalpy calculations assume.

Unknown bond enthalpies can be calculated given the enthalpy change for a reaction involving the compound which includes the bond, together with other relevant bond enthalpies.

Example

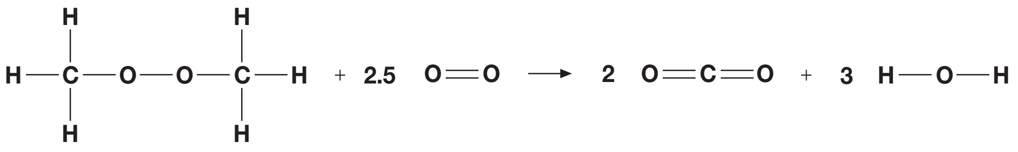
Calculate a value for the bond enthalpy for the O–O bond in the gas dimethyl peroxide, CH_3OOCH_3, given that the standard enthalpy of combustion, $\Delta_c H^\ominus[CH_3OOCH_3(g)] = -1460\,\mathrm{kJ\,mol^{-1}}$.

Note on the method

Write the equation for the reaction, showing the molecules and the bonds, so that you can count the number of bonds broken and formed. Look up the known bond enthalpy values from the data sheet for Chapter 8, which you can access via the QR code for this chapter on page 313.

Let the unknown bond enthalpy term be x. Equate the known enthalpy change for the reaction with the enthalpy change calculated from bond enthalpies, including the unknown value. Then rearrange the equation to find the value of x.

Answer



$$\mathrm{H_3C{-}O{-}O{-}CH_3} + 2.5\ \mathrm{O{=}O} \longrightarrow 2\ \mathrm{O{=}C{=}O} + 3\ \mathrm{H{-}O{-}H}$$

Bonds broken (endothermic)	Total energy change/ kJ mol^{-1}	Bonds formed	Total energy change/ kJ mol^{-1}
6 × C–H	+(6 × 413) = 2478	6 × O–H	−(6 × 464) = 2784
2 × C–O	+(2 × 336) = 672	4 × C=O	−(4 × 805) = 3220
2.5 × O=O	+(2.5 × 498) = 1245		
1 × O–O	+ x		

$\Delta_c H^{\ominus}[CH_3OOCH_3(g)] = -1460\,kJ\,mol^{-1}$

$= +(2478 + 672 + 1245 + x)\,kJ\,mol^{-1} - (2784 + 3220)\,kJ\,mol^{-1}$

$-1460\,kJ\,mol^{-1} = +4395\,kJ\,mol^{-1} + x - 6004\,kJ\,mol^{-1}$

$x = -1460\,kJ\,mol^{-1} - 4395\,kJ\,mol^{-1} + 6004\,kJ\,mol^{-1} = 149\,kJ\,mol^{-1}$

$E(O–O)$ in dimethyl peroxide = + 149 kJ mol^{-1}

Test yourself

Where relevant, refer to the data sheet for Chapter 8, 'Mean bond enthalpies and bond lengths', which you can access via the QR code for this chapter on page 313, to help you answer these questions.

15 **a)** Look back at Figure 8.20 and write out the equation

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

showing all the bonds between atoms in the molecules.

b) Refer to the data sheet of mean bond enthalpies and calculate:

i) the energy needed to break one mole of O=O bonds plus two moles of H–H bonds

ii) the energy given out when four moles of O–H bonds are formed in two moles of water (steam) molecules

iii) the energy released during the reaction to form two moles of water (steam).

16 Look up the bond enthalpies for the H–H, Cl–Cl and H–Cl bonds.

a) Calculate the overall enthalpy change for this reaction.

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

b) Draw an energy level diagram for the reaction (similar to Figure 8.20).

17 **a)** Calculate the average of the successive bond enthalpies for the two O–H bonds in water mentioned in Section 8.7.

b) Compare your answer with the mean bond enthalpy of the O–H bond given in the table of mean bond enthalpies.

18 **a)** Make a table to show the mean bond enthalpies and bond lengths of the C–C, C=C and C≡C bonds.

b) What generalisations can you make based on your table?

19 Use mean bond enthalpies to estimate the enthalpy change when ethene, $H_2C{=}CH_2(g)$, reacts with $H_2(g)$ to form ethane, $CH_3{–}CH_3(g)$.

20 **a)** Which are likely to give a more accurate answer to a calculation of the enthalpy change for a reaction – mean bond enthalpies or enthalpies of formation?

b) Give a reason for your answer to part (a).

21 Look carefully at the mean bond enthalpies for hydrogen and the halogens (fluorine, chlorine, bromine and iodine).

a) Write an equation for the reaction of hydrogen with chlorine.

b) Explain which bond (H–H or Cl–Cl) you think will break first in the reaction.

c) How would you expect the reaction of fluorine with hydrogen to compare with the reaction of chlorine with hydrogen?

Exam practice questions

1 a) Draw and label a diagram of the apparatus that you could use to determine the enthalpy change of the reaction between powdered magnesium and excess copper(II) sulfate solution. *(3)*

b) When excess powdered magnesium was added to $50\,cm^3$ of $0.040\,mol\,dm^{-3}$ copper(II) sulfate solution, the temperature rose by 5.0 °C.

- **i)** Write a balanced equation with state symbols for the reaction. *(1)*
- **ii)** Calculate the energy transferred to the copper(II) sulfate solution. *(2)*
- **iii)** What assumptions have you made in your calculation in part (ii)? *(2)*
- **iv)** Calculate the enthalpy change for the reaction shown in your equation in part (i). *(3)*

2 A butane gas burner is used to heat water. The standard enthalpy of combustion of butane gas, $\Delta_c H^\ominus = -2876\,kJ\,mol^{-1}$. The specific heat capacity of water = $4.18\,J\,g^{-}\,K^{-1}$.

a) How much energy is needed to heat 500 g of water from 20 °C to its boiling point? *(1)*

b) How much butane, in moles, must burn to supply the energy needed? *(1)*

c) What volume of butane gas is needed, measured under conditions such that its molar volume is $24.0\,dm^3\,mol^{-1}$? *(1)*

d) What assumptions have you made in answering this question? *(2)*

3 An excess of solid sodium hydrogencarbonate was added to $50\,cm^3$ of $1.0\,mol\,dm^{-3}$ ethanoic acid in an insulated polystyrene container under standard conditions. The temperature fell by 8.0 °C.

a) Complete the following equation for the reaction.

$$CH_3COOH(aq) + NaHCO_3(s) \rightarrow \_\_\_\_ + \_\_\_\_ + \_\_\_\_$$ *(2)*

b) Why do you think the $NaHCO_3$ was added in small portions? *(1)*

c) Calculate the energy change during the reaction. (Assume that the specific heat capacity of the solution is $4.18\,J\,g^{-1}\,K^{-1}$ and its density is $1.0\,g\,cm^{-3}$. Ignore the mass of sodium hydrogencarbonate.) *(2)*

d) How many moles of ethanoic acid were used? *(1)*

e) Calculate the standard enthalpy change of the reaction. Show the correct sign and units. *(3)*

f) Explain the number of significant figures in your answer. *(1)*

4 Hydrogen reacts with oxygen to form water or steam depending on the conditions.

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^\ominus = -286\,kJ\,mol^{-1}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \Delta H^\ominus = -242\,kJ\,mol^{-1}$$

a) On the same diagram draw energy level diagrams to represent these two changes *(3)*

b) Use the diagram in (a) to work out the enthalpy change for water turning to steam. *(2)*

$$H_2O(l) \rightarrow H_2O(g)$$

5 a) Give a definition of the term 'standard enthalpy change of combustion'. *(3)*

b) Write an equation for the change for which the enthalpy change is the standard enthalpy of combustion of propane. *(2)*

c) Give a definition of the term 'standard enthalpy change of formation'. *(3)*

d) Write an equation for the change for which the enthalpy change is the standard enthalpy change of formation of propanal. *(2)*

6 When gypsum($CaSO_4.2H_2O(s)$) is heated very strongly, it decomposes forming the anhydrous salt (anhydrite) and water.

a) Write a balanced equation with state symbols for the decomposition of gypsum. *(2)*

b) Is the decomposition likely to be exothermic or endothermic? Explain your answer. *(2)*

c) Why can the enthalpy change for the decomposition of gypsum **not** be measured directly? *(1)*

d) Using the following values, calculate the standard enthalpy change for the decomposition. *(5)*

$$\Delta_f H^\ominus[CaSO_4.2H_2O(s)] = -2023\,kJ\,mol^{-1}$$

$$\Delta_f H^\ominus[CaSO_4(s)] = -1434\,kJ\,mol^{-1}$$

$$\Delta_f H^\ominus[H_2O(l)] = -286\,kJ\,mol^{-1}$$

7 Tin is manufactured by heating tinstone, SnO_2, at high temperatures with coke (carbon).

There are two possible reactions for the process.

Reaction 1: $SnO_2(s) + C(s) \rightarrow Sn(s) + CO_2(g)$

Reaction 2: $SnO_2(s) + 2C(s) \rightarrow Sn(s) + 2CO(g)$

a) Calculate the standard enthalpy change for each of the possible reactions using the data below.

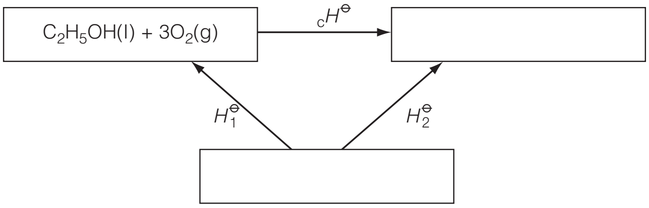
$\Delta_f H^\ominus[SnO_2(s)] = -581\,kJ\,mol^{-1}$

$\Delta_f H^\ominus[CO_2(g)] = -394\,kJ\,mol^{-1}$

$\Delta_f H^\ominus[CO(g)] = -110\,kJ\,mol^{-1}$ *(6)*

b) Use your calculations to explain which of the reactions would be most economic for industry. *(2)*

8 The Hess cycle below can be used to calculate the standard enthalpy change of combustion of ethanol, $\Delta_c H^\ominus$, using standard enthalpy changes of formation.



a) i) Copy and complete the cycle by filling in the empty boxes. *(2)*

ii) Define the term 'standard enthalpy change of formation' of a compound. *(3)*

iii) Use the Hess cycle to calculate the standard enthalpy change of combustion of ethanol, $\Delta_c H^\ominus$. Use this data:

$\Delta_f H^\ominus[CO_2(g)] = -394\,kJ\,mol^{-1}$

$\Delta_f H^\ominus[H_2O(l)] = -286\,kJ\,mol^{-1}$

$\Delta_f H^\ominus[C_2H_5OH(l)] = -277\,kJ\,mol^{-1}$ *(6)*

b) A student carried out an experiment, using the apparatus shown in Figure 8.7 on page 240, to estimate the standard enthalpy change of combustion of ethanol. The apparatus was surrounded with a screen to reduce draughts. The student added 150 g water to the metal can. After the burner had heated the can and water for a few minutes the temperature of the water had risen by 14.8 °C. The mass of the alcohol that had burned was 0.898 g.

i) Calculate the energy transferred to the water. (The specific heat capacity of water is $4.18\,J\,g^{-1}\,K^{-1}$.) *(2)*

ii) Calculate an experimental value for the standard enthalpy change of combustion. Give your answer to an appropriate number of significant figures. *(3)*

iii) Compare your answers to (a)(iii) and (b)(ii). Suggest reasons to explain the difference in the values. *(2)*

9 Butane (Camping Gaz®), C_4H_{10}, burns readily on a camp cooker. The equation for the reaction is:

$$C_4H_{10}(g) + 6\tfrac{1}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$$

a) Rewrite the equation showing all the covalent bonds between atoms in the reactants and products. *(4)*

b) Make a table showing the bonds broken in the reactants and the bonds formed in the products during the reaction. *(2)*

c) Use the following mean bond enthalpies to calculate the enthalpy change of the reaction. *(4)*

$E(C\text{–}C) = 347\,kJ\,mol^{-1}$

$E(C\text{–}H) = 413\,kJ\,mol^{-1}$

$E(O{=}O) = 498\,kJ\,mol^{-1}$

$E(C{=}O) = 805\,kJ\,mol^{-1}$

$E(H\text{–}O) = 464\,kJ\,mol^{-1}$

d) Give two reasons why the value calculated in part (c) is not the same as the standard enthalpy change of the reaction calculated at 298 K. *(2)*

10 A student suggested that ethane might react with bromine vapour in two different ways in bright sunlight.

Reaction 1: $C_2H_6(g) + Br_2(g) \rightarrow C_2H_5Br(g) + HBr(g)$

Reaction 2: $C_2H_6(g) + Br_2(g) \rightarrow 2CH_3Br(g)$

a) Use the following mean bond enthalpies to calculate the enthalpy changes for the two possible reactions.

$E(\text{C–C}) = 347\,\text{kJ mol}^{-1}$

$E(\text{Br–Br}) = 193\,\text{kJ mol}^{-1}$

$E(\text{C–H}) = 413\,\text{kJ mol}^{-1}$

$E(\text{H–Br}) = 366\,\text{kJ mol}^{-1}$

$E(\text{C–Br}) = 290\,\text{kJ mol}^{-1}$ *(6)*

b) Can you explain from the data, and your calculation, why Reaction 1 is the one that is found to occur? *(2)*

c) Suggest two reasons why your calculated enthalpy changes may not agree with the accurately determined experimental values. *(2)*

11 Hex-1-ene reacts with hydrogen gas to form hexane. Hex-1-ene and hexane are liquids under standard conditions.

a) i) Write an equation of the reaction of hex-1-ene with hydrogen and state the catalyst used for the reaction. *(2)*

ii) Draw a Hess's Law cycle to show how the standard enthalpy change for the reaction of hex-1-ene with hydrogen can be calculated from these enthalpy changes of combustion:

$\Delta_c H^{\ominus}[C_6H_{12}(l)] = -4003\,\text{kJ mol}^{-1}$

$\Delta_c H^{\ominus}[H_2(g)] = -286\,\text{kJ mol}^{-1}$

$\Delta_c H^{\ominus}[C_6H_{14}(g)] = -4163\,\text{kJ mol}^{-1}$ *(3)*

iii) Use your cycle to calculate $\Delta H^{\ominus}_{\text{reaction}}$. *(3)*

b) The table below shows the enthalpy change for three other alkenes with hydrogen.

Reaction	**Standard enthalpy change of reaction /kJ mol^{-1}**
propene + hydrogen → propane	–125
but-1-ene + hydrogen → butane	–126
pent-1-ene + hydrogen → pentane	–126

Explain why the values for the enthalpy change for the reaction of these alkenes with hydrogen are so similar. *(3)*

12 Octane is typical of the hydrocarbons found in petrol made from crude oil.

Most methanol is still made from the methane in natural gas but a growing amount of methanol is being made from other resources. Methanol can be produced from anything that is, or ever was, a plant. This includes biomass, agricultural and timber waste, solid municipal waste, landfill gas, industrial waste and pollution and a number of other feedstocks.

In some instances it is important to choose a fuel based on the energy released per gram when the fuel burns.

It can also be important to compare the energy released per cm^3 of fuel.

Fuel	**Density/g cm^{-3}**	**$\Delta_c H^{\ominus}$(298 K) /kJ mol^{-1}**
Methanol	0.793	–726
Octane	0.703	–5470

a) i) Give an example where it might be important to choose a fuel giving the higher energy per gram. *(1)*

ii) Calculate the standard enthalpy change of combustion per gram for methanol and octane and comment on the values. *(2)*

b) i) Give an example where it might be important to choose a fuel giving the higher energy per cm^3. *(1)*

ii) Calculate the standard enthalpy change of combustion per cm^3 for methanol and octane. *(2)*

c) Discuss the advantages and disadvantages of octane and methanol as fuels, taking into account your answers to parts (a) and (b) and the information at the start of this question. *(6)*

9 Kinetics I

9.1 Reaction rates

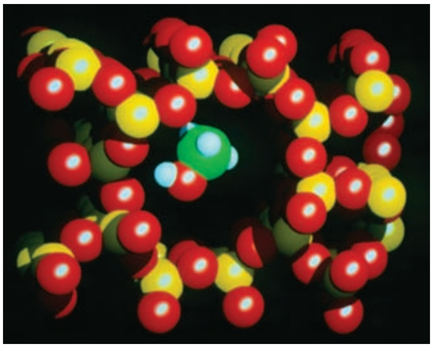


Figure 9.1 Computer graphics showing a molecule of methanol (with green carbon atom) passing through a channel in the synthetic zeolite catalyst. This catalyst is used to make a new fuel from methanol. Chemists carry out research to understand reactions on an atomic scale so that they can develop more effective catalysts.

The study of rates of reaction is important because it helps chemists to control reactions both in the laboratory and on a large scale in industry. Chemists have a model for explaining the effects of the various factors that affect the rates of reactions. This model helps them to understand what happens to atoms, molecules and ions during chemical changes.

In the chemical industry, manufacturers aim to get the best possible yield in the shortest time. The development of new catalysts to speed up reactions is, therefore, one of the frontier aspects of modern chemistry (Figure 9.1). The aim is to make manufacturing processes more efficient so that they use less energy and produce little or no harmful waste. The need for greater efficiency in chemical processes is now more pressing than ever as people become more aware of the harm that waste chemicals can do to our health and to the environment.

The study of reaction rates is called **chemical kinetics** which is important in many other fields. The study of rates of reaction helped environmental scientists, for example, to explain why CFCs and other chemicals are destroying the ozone layer in the upper atmosphere. Pharmacologists who study the chemistry of drugs must study the speed at which they change to other chemicals or break down in the human body. Then the pharmacists who formulate and supply medicines need to know about the rate at which the chemicals slowly degrade in the bottle or pack. For many medicines, the shelf life is the time for which they can be stored before the concentration of the active ingredient has dropped by 10%.

Key term

Chemical kinetics is the study of the rates of chemical reactions.

Chemical reactions happen at a variety of speeds (Figure 9.2). Ionic precipitation reactions are very fast and explosions are even faster. However, the rusting of iron and other corrosion processes are slow and may continue for years.

Figure 9.2 Firefighters have to know how to slow down and stop burning. Water cools the burning materials as it evaporates and the steam produced can help to keep out the air.

Test yourself

1 How would you slow down or stop these reactions:
   - a) iron corroding
   - b) toast burning
   - c) milk turning sour?

2 How would you speed up these reactions:
   - a) fermentation in dough to make the bread rise
   - b) solid fuel burning in a stove
   - c) epoxy glue (adhesive) setting
   - d) the conversion of chemicals in engine exhausts to harmless gases?

9.2 Measuring reaction rates

Balanced chemical equations give no information about how quickly the reactions occur. In order to get this information, chemists have to do experiments to measure the rates of reactions under various conditions.

The amounts of the reactants and products change during any chemical reaction – products form as reactants disappear. The rates at which these changes happen give a measure of the **rate of reaction**.

Key term

The **rate of reaction** is found by measuring the rate of formation of a product or the rate of removal of a reactant. The usual procedure for finding the rate is to measure some property of the reaction mixture, such as its volume, and to see how this property varies with time.

The rate of the reaction between magnesium and hydrochloric acid

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

can be measured by:

- the rate of loss of magnesium
- the rate of loss of hydrochloric acid
- the rate of formation of magnesium chloride
- the rate of formation of hydrogen.

In this example, it is probably easiest to measure the rate of formation of hydrogen by collecting the gas and recording its volume with time (Figure 9.3).

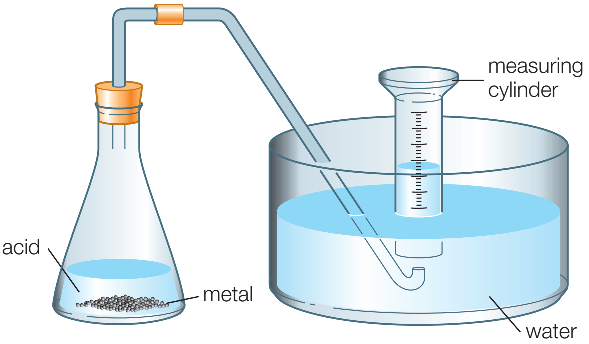


Figure 9.3 Collecting and measuring the gas produced when magnesium reacts with acid. A gas syringe can be used instead of a measuring cylinder full of water.

Chemists design their rate experiments to measure a property which changes with the amount or concentration of a reactant or product. Then:

$$\text{rate of reaction} = \frac{\text{change recorded in the property}}{\text{time for the change}}$$

Test yourself

3 In an experiment to study the reaction of magnesium with dilute hydrochloric acid, 48 cm^3 of hydrogen forms in 10 s at room temperature. Calculate the average rate of formation of:

- **a)** hydrogen in cm^3 s^{-1}
- **b)** hydrogen in mol s^{-1} (Section 5.3)
- **c)** the rates of appearance or disappearance of the other product and the reactants in mol s^{-1}.

In most chemical reactions the rate changes with time. The graph in Figure 9.4 is a plot of the results from a study of the reaction of magnesium with dilute hydrochloric acid. The graph is steepest at the start, when the reaction is at its fastest. As the reaction continues it slows down, until it finally stops. This happens because one of the reactants is being used up until none of it is left. The gradient at any point on a graph showing amount or concentration plotted against time measures the rate of reaction (Figure 9.5).

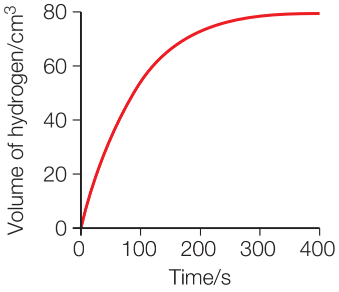


Figure 9.4 Volume of hydrogen plotted against time for the reaction of magnesium with hydrochloric acid.

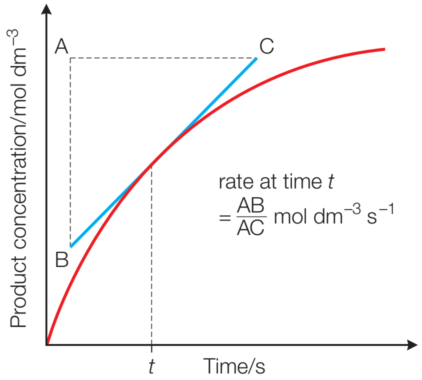


Figure 9.5 Graph showing the concentration of a product plotted against time. The gradient at any point measures the rate of reaction at that time.

A useful way of studying the effect of changing the conditions on the rate of a reaction is to find a way of measuring the rate just after mixing the reactants. Figure 9.6 is a graph for two different sets of conditions. When one of the reactants was more concentrated, line A was produced. Near the start, it took t_A seconds to produce x mol of product. When the same reactant was less concentrated, the results gave line B. This time, near the start it took t_B seconds to produce x mol of product. The reaction was slower when the concentration was lower, so it took longer to produce x mol of product.

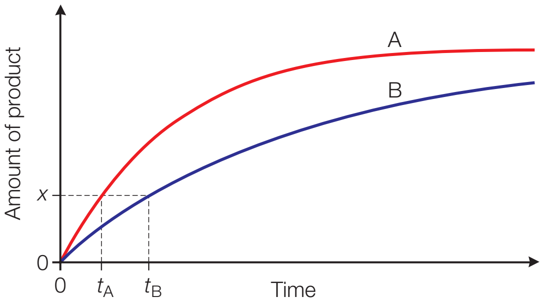


Figure 9.6 Formation of the same amount (x mol) of product starting with different concentrations of one of the reactants.

The average rate of formation of product on line A $= \frac{x}{t_A}$

The average rate of formation of product on line B $= \frac{x}{t_B}$

If x is kept the same, it follows that the average rate near the start $\propto \frac{1}{t}$

This means that it is possible to arrive at a measure of the initial rate of a reaction by measuring how long the reaction takes to produce a small fixed amount of product, or use up a small fixed amount of reactant.

9.3 What factors affect reaction rates?

Concentration

In general, the higher the concentration of the reactants, the faster the reaction. For gas reactions, a change in pressure has the same effect as changing the concentration – a higher pressure compresses a mixture of gases and increases their concentration. So, in a mixture of reacting gases, the higher the pressure, the faster the reaction.

Activity

Investigation of the effect of concentration on the rate of a reaction

Figure 9.7 illustrates an investigation of the effect of concentration on the rate at which thiosulfate ions in solution react with hydrogen ions to form a precipitate of sulfur.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(aq) + H_2O(l)$$

The observer records the time taken for the sulfur precipitate to obscure the cross on the paper under the flask. In this example, the quantity x in Figure 9.6 is the amount of sulfur needed to hide the cross on the paper. This is the same each time – so, the rate of reaction is proportional to $1/t$. The results of the investigation are shown in Table 9.1.

1 Which factors must be kept constant in this investigation to ensure that the results are valid? Explain your answer.

2 How would you prepare 50 cm^3 of a solution of sodium thiosulfate solution with a concentration of 0.12 mol dm^{-3} from a solution with a concentration of 0.15 mol dm^{-3}?

3 Suggest why the mixture in the flask should be poured into a container of saturated sodium carbonate solution after each experiment.

4 The pale yellow precipitate of sulfur often sticks to the flask forming a thin film on the glass surface. Why is it important to thoroughly clean the flask after each experiment?

5 Calculate the value for the rate of reaction when the concentration of thiosulfate ions is 0.12 mol dm^{-3}.

6 Plot a graph to show how the rate of reaction varies with the concentration of thiosulfate ions.

7 What is the relationship between reaction rate and concentration of thiosulfate for this reaction according to your graph?

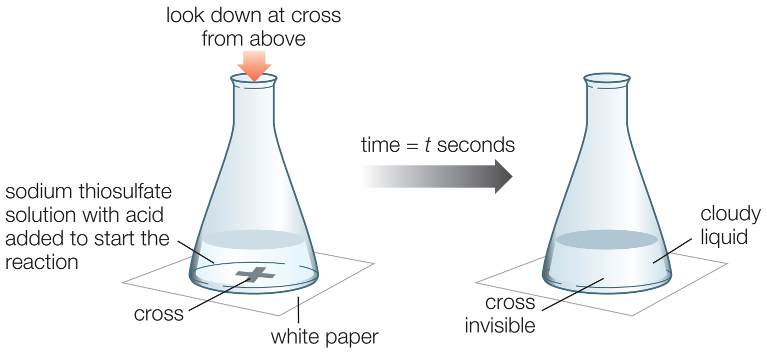

look down at cross from above
time = t seconds
sodium thiosulfate solution with acid added to start the reaction
cloudy liquid
cross
white paper
cross invisible

Figure 9.7 Investigating the effect of the concentration of thiosulfate ions on the rate of reaction in acid solution. The hydrogen ion concentration is the same in each experiment.

Table 9.1 Results of the investigation in Figure 9.7.

Experiment	Concentration of thiosulfate ions/ mol dm^{-3}	Time, t, for the cross to be obscured/s	Rate of reaction, $\frac{1}{t}$/s^{-1}
1	0.15	43	0.023
2	0.12	55	
3	0.09	66	0.015
4	0.06	105	0.0095
5	0.03	243	0.0041

Surface area of solids

Breaking a solid into smaller pieces increases the surface area in contact with a liquid or gas. This speeds up any reaction happening at the surface of the solid. This effect also applies to reactions between liquids which do not mix. Shaking breaks up one liquid into droplets which are then dispersed in the other liquid, thereby increasing the surface area for reaction.

Activity

Investigating the effect of surface area on the rate of a reaction

Figure 9.8 illustrates an investigation of the rate of reaction of lumps of calcium carbonate (marble) with dilute nitric acid. The results are given in Table 9.2. Both sets of results were obtained using 20 g of marble chips and 40 cm^3 of 2.0 mol dm^{-3} nitric acid. The marble was in excess.

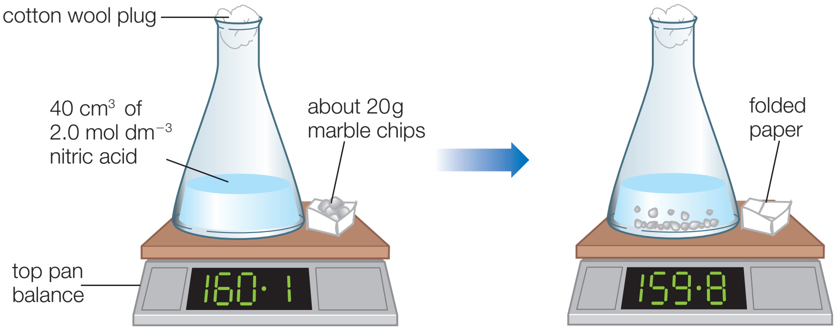


Figure 9.8 Apparatus for comparing the reaction rate of calcium carbonate with nitric acid.

1 **a)** Explain why all the equipment and chemicals were placed together on the balance throughout the experiment, as shown in Figure 9.8.
  b) Why was a cotton wool plug placed in the neck of the flask?
2 Plot the two sets of results on the same axes.
3 Work out the initial rates of the two reactions by drawing tangents and determining the gradients.
4 **a)** After what time did the reaction stop for each set of results?
  b) Why did the reaction stop?
5 Why was the same mass of carbon dioxide formed in both sets of results?
6 For a given mass of marble, how is surface area related to particle size?
7 What is the effect on this reaction of changing the surface area of the solid?
8 Sketch on your graph the results you would expect if you repeated the experiment with 20 g small marble chips and 40 cm^3 of 1.0 mol dm^{-3} nitric acid.
9 **a)** Use the equation for the reaction to calculate the theoretical mass of carbon dioxide formed when 40 cm^3 of 2.0 mol dm^{-3} nitric acid reacts completely with calcium carbonate.
  b) Suggest reasons for the difference between the actual and the theoretical mass of carbon dioxide formed.

Table 9.2 Results of experiments to compare the reaction rate of calcium carbonate with nitric acid using the same mass of larger and smaller marble chips.

Time/s	Mass of carbon dioxide formed/g	
	Small marble chips	Large marble chips
30	0.45	0.18
60	0.85	0.38
90	1.13	0.47
120	1.31	0.75
180	1.48	1.05
240	1.54	1.25
300	1.56	1.38
360	1.58	1.47
420	1.59	1.53
480	1.60	1.57
540	1.60	1.59
600	1.60	1.60

Temperature

Raising the temperature is a very effective way of increasing the rate of a reaction. For a number of chemical reactions at around room temperature, a 10 °C rise in temperature roughly doubles the rate of reaction (see Figure 9.9).

Bunsen burners, hot-plates and heating mantles are common items of equipment in laboratories because it is often convenient to speed up reactions by heating the reactants. For the same reason, many industrial processes are carried out at high temperatures.

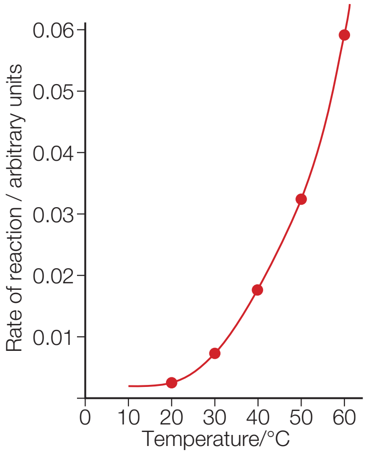


Figure 9.9 The effect of temperature on the rate of decomposition of thiosulfate ions to form sulfur.

Catalysts

Catalysts have an astonishing ability to speed up the rates of some chemical reactions without themselves changing permanently. Very small quantities of active catalysts can speed reactions to produce many times their own mass of chemicals.

Catalysts work by removing or lowering the barriers preventing reaction – they bring reactants together in a way that makes a reaction more likely.

Some catalysts such as nickel metal can catalyse many different reactions. However, catalysts can also be extraordinarily selective – a catalyst may increase the rate of only one very specific reaction. Enzymes, the catalysts in living cells, are especially selective.

Catalysts change the **mechanisms of reactions**, but they are not reactants and they do not appear in the overall chemical equation. In theory, catalysts can be used over and over again, but in practice there is some loss of catalyst. Sometimes catalysts become contaminated, sometimes they are hard to recover completely from the products and sometimes the catalyst changes its state, such as from lumps to a fine powder, which means that it is no longer useable.

Most industrial processes involve passing a mixture of gases over a solid catalyst. Such catalysts are described as **heterogeneous catalysts** because the reactants and catalyst are in different **phases**. The gas molecules are briefly held onto the surface of the solid, where the atoms of the catalyst help them to react; then the product molecules break free and are carried away in the flow of gas.

One of the targets in the modern chemical industry is to develop catalysts that make manufacturing processes more efficient, so that they produce less waste and use less energy. A novel catalyst can make possible a new route for making a chemical product that has a higher atom economy. Developing a new catalyst can also make it possible to carry out a reaction at a lower temperature or at a lower pressure. This saves fuel. The cost of fuel is one of the factors that determines the profitability of large-scale chemical processes.

Test yourself

4 a) Use the Haber process for making ammonia to explain what is meant by a heterogeneous catalyst.

b) Suggest advantages of using heterogeneous catalysts in industry.

Key terms

A **catalyst** speeds up the rate of a chemical reaction without itself changing to a different substance. The catalyst can often be recovered at the end of the reaction. A small amount of catalyst can be effective.

The **mechanism of a reaction** is a description of how a reaction takes place showing, step by step, the bonds which break and the new bonds which form as reactants turn into products.

A **phase** is one of the three states of matter – solid, liquid or gas. Chemical systems often have more than one phase. Each phase is distinct but need not be pure. For example, a solid in equilibrium with its saturated solution is a two-phase system. In the reactor for ammonia manufacture, the mixture of nitrogen, hydrogen and ammonia gases make up one phase with the iron catalyst being a separate solid phase.

A **heterogeneous catalyst** is one that is in a different phase from the reactants. Generally a heterogeneous catalyst is a solid while the reactants are gases, or in solution.

9.4 Collision theory

Scientists can explain the factors that affect reaction rates. They use a model which gives a picture of what happens to atoms, molecules and ions as they react. This model works best for gases but it can also be applied to reactions in solution.

Gas molecules in motion

The model that scientists use to explain the behaviour of gases assumes that the molecules in a gas are in rapid random motion and colliding with each other. They call this particles-in-motion model the ‘kinetic theory’. The name comes from a Greek word for movement.

The kinetic theory makes a number of assumptions about the molecules of a gas. Applying Newton’s laws of motion to the collection of particles leads to equations that can describe the properties of gases very accurately.

The assumptions of the kinetic theory model are that:

- gas pressure results from the collisions of the molecules with the walls of the container
- there is no loss of energy in the elastic collisions between the molecules and the walls of any container
- the molecules are so far apart that the volume of the molecules can be neglected in comparison with the total volume of gas
- the molecules do not attract each other
- the average kinetic energy of molecules is proportional to their temperature on the Kelvin scale.

A gas that behaves exactly as this model predicts, obeying the gas laws, is called an ‘ideal gas’ (Section 5.3). Real gases do not behave exactly like this.

The assumptions built into the model help to explain why real gases approach ideal behaviour at high temperatures and low pressures:

- at high temperatures, the molecules are moving so fast that any small attractive forces between them can be ignored
- at low pressures the volumes are so big that the space taken up by the molecules is insignificant.

This kinetic theory also helps to explain why real gases deviate from ideal gas behaviour as they get nearer to becoming a liquid. As a gas liquefies, the molecules get very close together and the volume of the molecules cannot be ignored. Also, gases could not liquefy unless there were some attractive (intermolecular) forces between the molecules to hold them together.

The Dutch physicist Johannes van der Waals (1837–1923) developed his theory of intermolecular forces (Section 2.6) by studying the behaviour of real gases and their deviations from the ideal gas behaviour.

The Maxwell–Boltzmann distribution

Two physicists used the kinetic theory to explore the distribution of energies among the molecules in gases. They worked out the proportion of molecules with a given energy at a particular temperature. The two physicists were James Maxwell (1831–1879) in Britain and Ludwig Boltzmann (1844–1906) in Austria.

Figure 9.10 shows the distribution of energies for the molecules of a gas under two sets of conditions. This **Maxwell–Boltzmann distribution** helps to explain the effects of temperature changes and catalysts on the rates of reactions.

Key term

The **Maxwell–Boltzmann distribution** shows the spread of molecular kinetic energies for a gas at a particular temperature. It shows that there is a wide spread of molecular energies and so the molecules are moving at different speeds.

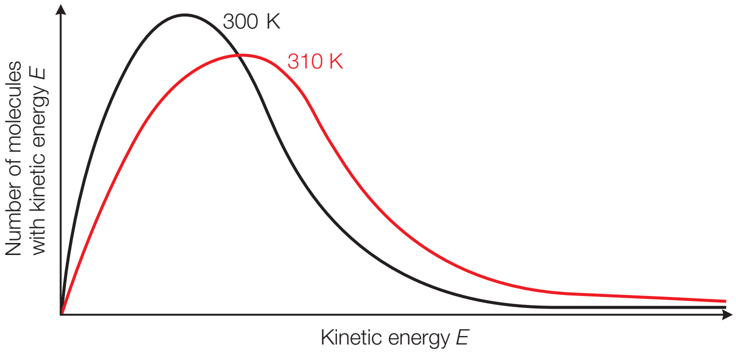


Figure 9.10 The Maxwell–Boltzmann distribution of kinetic energies of the molecules of a gas at two temperatures. The area under the curve gives the total number of molecules. This area does not change as the temperature rises, so the peak height falls as the temperature rises and the curve spreads to the right.

Explaining the effects of concentration, pressure and surface area on reaction rates

In any reaction mixture the billions of atoms, molecules or ions are forever bumping into each other. When they collide there is a chance that they will react.

Raising the pressure of a gas means that the reacting particles are closer together. There are more frequent collisions and, therefore, the reaction goes faster. Increasing the concentration of reactants in solution has a similar effect (Figure 9.11).

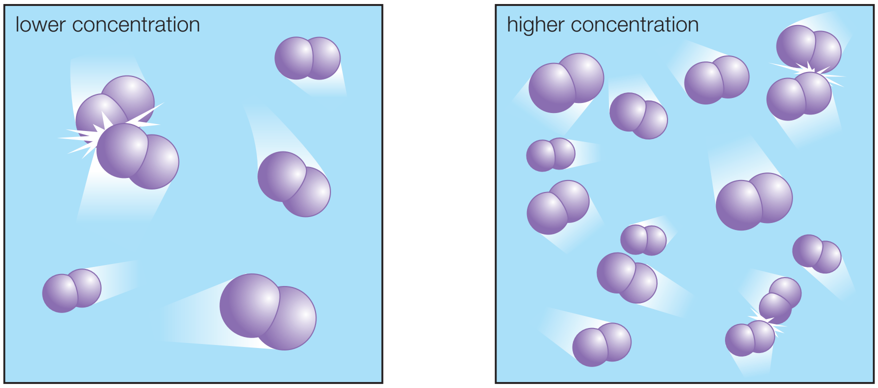


Figure 9.11 Raising the pressure, or concentration, means that the reacting atoms, molecules or ions are closer together. There are more frequent collisions and the reaction is faster.

In a reaction of a solid with either a liquid or a gas, the reaction is faster if the solid is broken up into smaller pieces. Crushing the solid increases its surface area – collisions can be more frequent and the rate of reaction is faster (Figure 9.12).

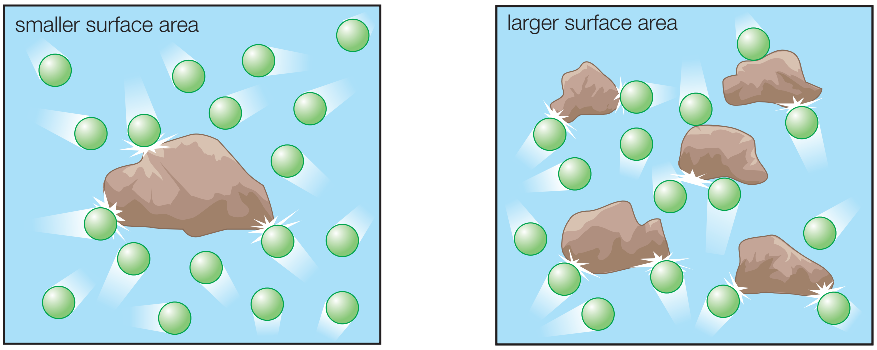


Figure 9.12 Breaking a solid into smaller pieces increases the surface area exposed to reacting chemicals in a gas or in solution. Note that this diagram shows the solid fragments and the molecules on different scales. In reactions of this kind, the fragments of solid are generally huge compared to the size of the molecules or ions.

Explaining the effects of temperature on reaction rates

It is not enough simply for the molecules to collide. Most collisions do not result in a reaction. Molecules simply bounce off each other if there is not enough energy in the collision to break bonds. Molecules may also fail to react if they are not angled correctly as they collide. Molecules are in such rapid motion that if every collision led to a reaction, most reactions would be explosive.

Chemists use the term **activation energy** to describe the minimum energy needed in a collision between molecules if they are to react. Activation energies account for the fact that reactions go much more slowly than would be expected if every collision between atoms and molecules led to a reaction. Only a very small proportion of collisions bring about chemical change. Molecules can only react if they collide with enough energy for bonds to stretch and then break so that new bonds can form. At around room temperature, only a minute proportion of molecules have enough energy to react.

Figure 9.13 shows that the energy of the colliding molecules is taken in to stretch bonds as a **transition state** forms. Then, as old bonds break and new bonds form, the energy is released to create products. The net energy change is the enthalpy change for the reaction.

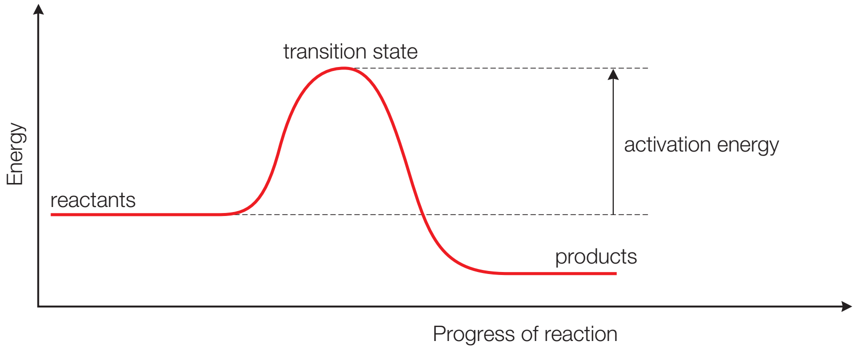
Key terms

The **activation energy** is the height of the energy barrier separating reactants and products during a chemical reaction. It is the minimum energy needed for a reaction between the amounts, in moles, shown in the equation for the reaction.

A **transition state** is the state of the reacting atoms, molecules or ions when they are at the top of the activation energy barrier for a reaction step. Transition states exist for such a brief moment that they cannot be detected or isolated.

A **reaction profile** is a graph which shows how the total enthalpy (energy) of the atoms, molecules or ions changes during the progress of a reaction from reactants to products.

Figure 9.13 **Reaction profile** showing the activation energy for a reaction.



The shaded areas in Figure 9.14 show the small proportions of molecules having enough energy to overcome the activation energy for a reaction at 300 K and 310 K. This area is larger at the higher temperature. So, at a higher temperature, more molecules have enough energy to react when they collide and the reaction goes faster. Also, when the molecules are moving faster, they collide more often.

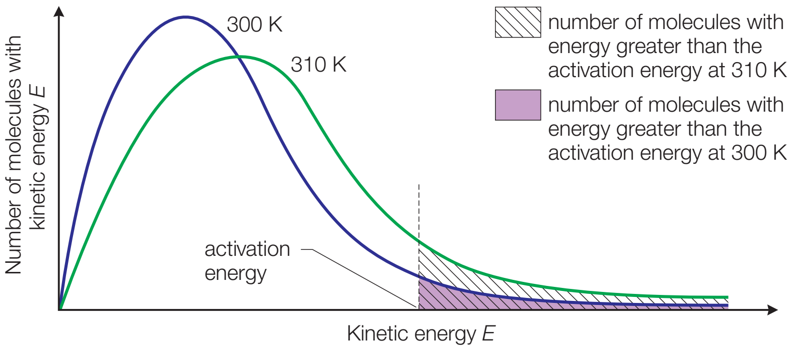


Figure 9.14 The Maxwell–Boltzmann distribution of kinetic energies in the molecules of a gas at 300 K and 310 K. The area under each curve is a measure of the number of molecules. At 310 K, more molecules have enough energy to react when they collide with other molecules.

Test yourself

5 Two factors explain why reactions go faster when the temperature rises. Identify these two factors in terms of the energy of molecules, atoms and ions.

Explaining the effects of catalysts on reaction rates

A catalyst works by providing an alternative pathway for the reaction with a lower activation energy. Lowering the activation energy increases the proportion of molecules with enough energy to react (Figure 9.15).

A catalyst changes the mechanism of a reaction and makes a reaction more productive by increasing the yield of the desired product and reducing waste.

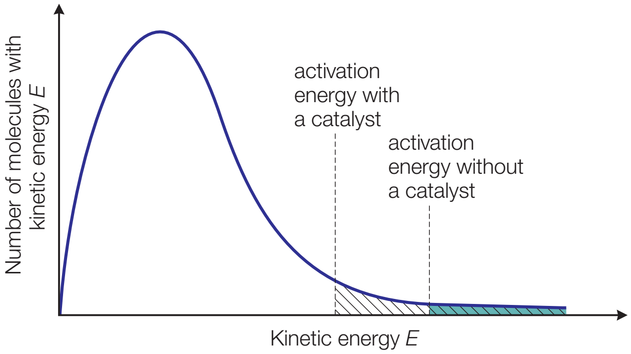


Figure 9.15 Distribution of molecular energies in a gas, showing how the proportion of molecules able to react increases when a catalyst lowers the activation energy.

Key term

Intermediates in reactions are atoms, molecules and ions which do not appear in the balanced equation but which are formed during one step of a reaction, then used up in the next step.

One of the ways in which a catalyst can change the mechanism of a reaction is to combine with the reactants to form an **intermediate**. The intermediate is a stage in the transition from reactants to products – it breaks down to give the products and the catalyst is released. This frees the catalyst to interact with further reactant molecules and the reaction continues (Figure 9.16).

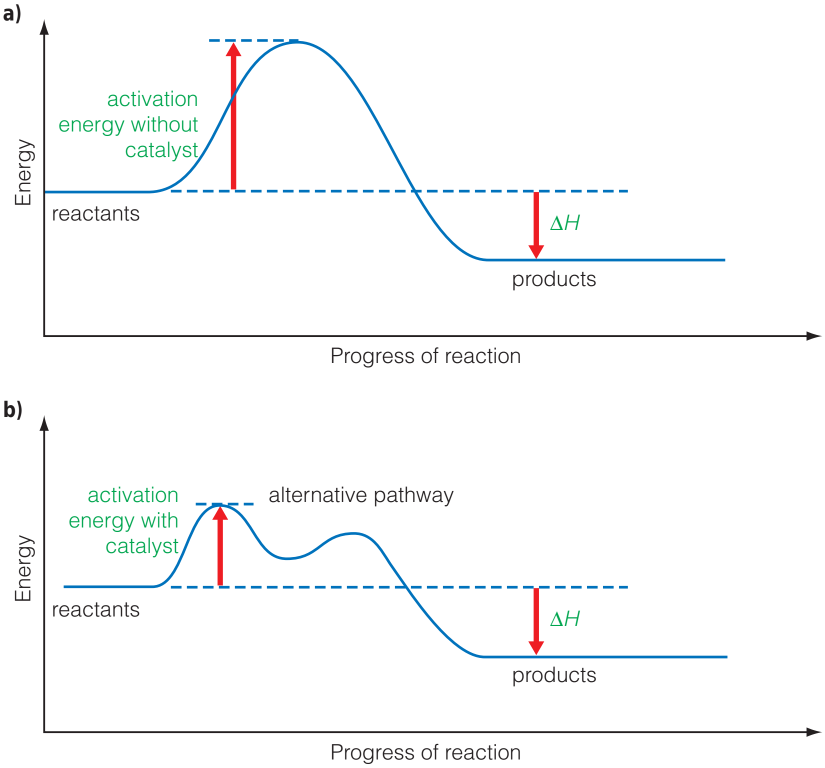


Figure 9.16 Reaction profiles for a reaction **a)** without a catalyst and **b)** with a catalyst. The dip in the curve of the pathway with a catalyst shows where an unstable intermediate forms.

Test yourself

6 Which parts of Figure 9.16 b show:
- **a)** the formation of an intermediate
- **b)** a transition state?

7 a) Why is a match or spark needed to light a Bunsen burner?
- **b)** Why does the gas keep burning once it has been lit?

8 Suggest a reason why catalysts are often specific for a particular reaction.

Exam practice questions

● 1 Hydrogen peroxide solution, $H_2O_2(aq)$, decomposes very slowly at room temperature releasing oxygen. The reaction is catalysed by manganese(IV) oxide. The table shows the volume of oxygen collected at regular intervals when one measure of MnO_2 powder is added to 50 cm^3 of a hydrogen peroxide solution at 20 °C.

a) Describe the apparatus that can be used to obtain the results in the table. Explain how the volume of gas can be measured accurately from the moment that the catalyst is added to the hydrogen peroxide solution. *(4)*

b) Write an equation for the reaction. *(1)*

c) Draw a graph of the results on axes with a vertical scale showing the volume of oxygen up to 100 cm^3. *(2)*

Time/s	Volume of oxygen/cm^3
0	0
20	10
40	20
60	26
80	32
100	35
120	38
140	39
160	40
180	40

d) Explain the shape of your graph. *(3)*

e) On the same axes, sketch the graphs you would expect if, in separate experiments, all the conditions are the same except that:

i) the temperature is raised to 40 °C

ii) the volume of hydrogen peroxide solution is 100 cm^3

iii) manganese(IV) oxide granules are used in place of powder

iv) the concentration of the hydrogen peroxide solution is halved. *(8)*

● 2 **a)** Explain why most collisions in a reaction mixture do not result in a reaction. *(2)*

b) How can the collision frequency between molecules in a gas be increased without changing the temperature? *(1)*

c) Why can a small increase in temperature lead to a large increase in the rate of a reaction? *(3)*

● 3 Sketch the reaction profile for a reaction taking place with a catalyst given that:

- the reaction is endothermic
- the activation energy for the formation of an intermediate is higher than the activation energy for the conversion of the intermediate to the products. *(3)*

● 4 **a)** Sketch a graph, with labelled axes, to show the Maxwell–Boltzmann distribution of the energies of the reactant molecules. *(2)*

b) Mark the energy axis to show a likely position for the activation energy of a reaction without a catalyst and with a catalyst. *(2)*

c) Use your graph to explain why a catalyst speeds up the rate of a reaction. *(3)*

● 5 Suggest explanations for these observations:

a) A mixture of oxygen and hydrogen gas does not react at room temperature. The mixture explodes if ignited with a spark or if a little powdered platinum is added. *(4)*

b) Nitrogen and oxygen do not usually react in the air but they do combine to give nitrogen monoxide in the cylinder of a car engine. *(4)*

c) There is a danger of explosions caused by dust in flour mills and coal mines. *(4)*

● 6 Some chemical reactions happen fast; others are very slow. What are the reasons for these differences? Illustrate your answer with examples. Use graphs and diagrams to enhance your explanations. *(6)*

● 7 Two important scientific models are the kinetic theory of gases and the collision theory of reaction rates. Identify key features of scientific models and show that they are illustrated by these examples. Discuss the importance and limitations of these examples of modelling. *(6)*

10

Equilibrium I

10.1 Reversible changes

The study of reversible reactions helps chemists to answer the questions 'How far?' and 'In which direction?' – questions they need to answer when trying to make new chemicals in laboratories and in industry.

Some changes go in only one direction – like baking bread. Once baked in an oven, there is no way to reverse the process and split a loaf back into flour, water and yeast. Burning a fuel, such as natural gas or petrol, is another example of a one-way process. Once these fuels have burned in air to make carbon dioxide and water, it is impossible to simply reverse the reaction to turn the products back to natural gas and petrol. The combustion of fuels is an irreversible process.

Many other reactions involve **reversible changes**. Haemoglobin, for example, combines with oxygen as red blood cells flow through the lungs, but then releases the oxygen for respiration as blood flows in the capillaries throughout the rest of the body. Another example is the reaction of water and dissolved carbon dioxide with the calcium carbonate of limestone. This reaction erodes limestone rock (Figure 10.1). The reaction is reversed in caves as stalactites form (Figure 10.2).

Key term

A **reversible change** is a process which can be reversed by altering the conditions.

Another example of a reversible reaction is the basis of a simple laboratory test for water. Hydrated cobalt(II) chloride is pink and so is a solution of the salt in water. Heating filter paper soaked in the solution in an oven makes

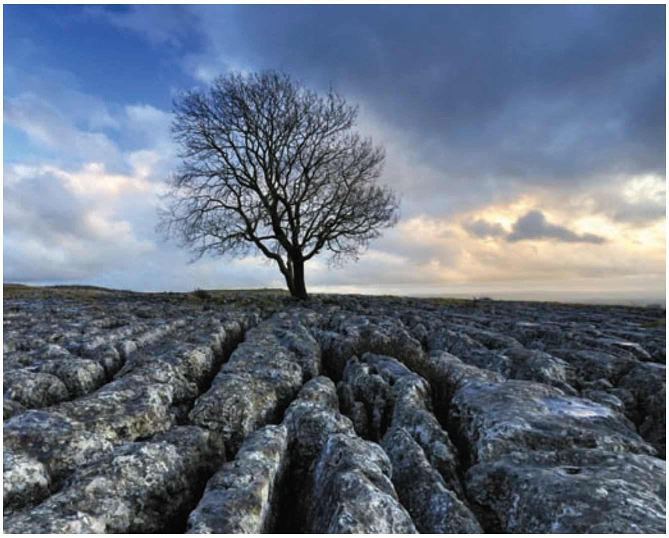


Figure 10.1 Eroded limestone rock near Malham in the Yorkshire Dales. The cracks in the limestone rock have been widened by natural chemical erosion. Rainwater made acid with dissolved carbon dioxide reacts with the calcium carbonate in limestone as the water flows over it.

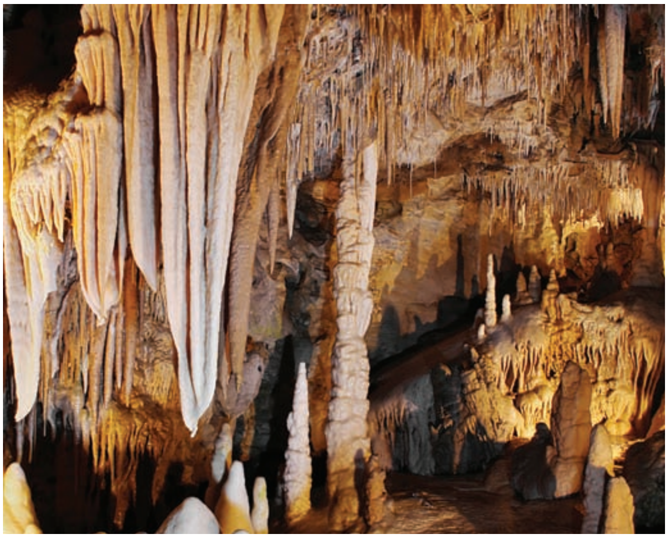


Figure 10.2 Stalactites and stalagmites in a cave. Stalactites and stalagmites form in limestone caves because the reaction of carbon dioxide and water with calcium carbonate is reversible. The reverse reaction reforms solid calcium carbonate.

the paper turn blue, because water is driven off from the solution leaving anhydrous cobalt(II) chloride on the paper.

$$\underset{\text{pink}}{CoCl_2.6H_2O(s)} \rightarrow \underset{\text{blue}}{CoCl_2(s)} + 6H_2O(g)$$

The blue paper provides a sensitive test for water as it turns pink again if exposed to water or water vapour. At room temperature water rehydrates the blue salt (Figure 10.3).

$$\underset{\text{blue}}{CoCl_2(s)} + 6H_2O(l) \rightarrow \underset{\text{pink}}{CoCl_2.6H_2O(s)}$$

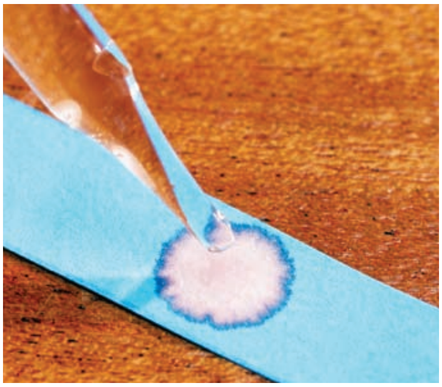


Figure 10.3 Using cobalt chloride paper to test for water.

The reaction of ammonia with hydrogen chloride is an example of a reaction in which the direction of change depends on the temperature. At room temperature, the two gases combine to make a white smoke of ammonium chloride.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

Heating reverses the reaction and ammonium chloride decomposes at high temperatures to give hydrogen chloride and ammonia.

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

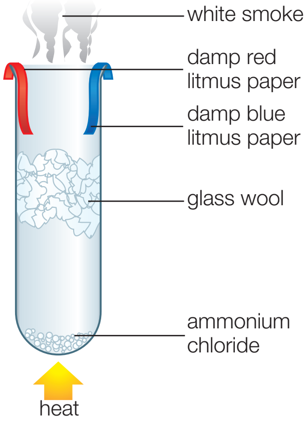


Figure 10.4 Investigating the thermal decomposition of ammonium chloride.

The apparatus in Figure 10.4 can be used to show that ammonium chloride decomposes into two gases on heating. Ammonia gas diffuses through the glass wool faster than hydrogen chloride. After a short time, the alkaline ammonia rises above the plug of glass wool and turns the red litmus blue. A while later both strips of litmus paper turn red as the acid hydrogen chloride arrives. A smoke of ammonium chloride appears above the tube when both gases meet and cool.

Changing the temperature is not the only way to alter the direction of change. Hot iron, for example, reacts with steam to make iron(III) oxide and hydrogen. Supplying plenty of steam and 'sweeping away' the hydrogen means that the reaction continues until all the iron changes to its oxide (Figure 10.5).

$$3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$$

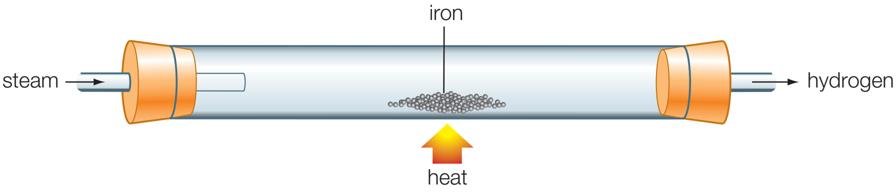


Figure 10.5 The forward reaction goes when the concentration of steam is high and the hydrogen is swept away, keeping its concentration low.

Tip

In an equation the chemicals on the left-hand side are the reactants – those on the right are the products. The 'left-to-right' reaction is the 'forward' reaction and the 'right-to-left' reaction is the backward reaction.

Altering the conditions brings about the reverse reaction. A stream of hydrogen reduces all the iron(III) oxide to iron, so long as the flow of hydrogen sweeps away the steam that has formed (Figure 10.6).

$$3Fe(s) + 4H_2O(g) \leftarrow Fe_3O_4(s) + 4H_2(g)$$

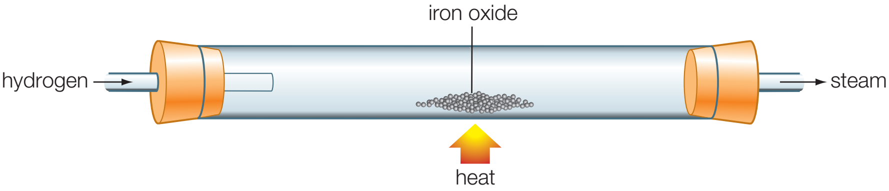


Figure 10.6 The reverse, or backward, reaction goes when the concentration of hydrogen is high and the steam is swept away, keeping its concentration low.

Test yourself

1 Write balanced equations, with state symbols, for the reactions when:

  a) rainwater and carbon dioxide erode calcium carbonate in limestone to form soluble calcium hydrogencarbonate

  b) aqueous calcium hydrogencarbonate decomposes to reform calcium carbonate as the solution drips from the roof of a cave.

2 How can the following changes be reversed, either by changing the temperature or by changing the concentration of a reactant or product:

  a) freezing water to ice

  b) changing blue litmus to its red form

  c) converting blue copper(II) sulfate to its white form?

3 Explain why wet washing does not dry if kept in a plastic laundry bag, but does dry if hung out on a line.

10.2 Reaching an equilibrium state

Reversible changes often reach a state of balance, or equilibrium. What is special about chemical equilibria is that nothing appears to be happening, but at a molecular level there is ceaseless change.

When chemists ask the question ‘How far?’, they want to know what the state of a reaction will be when it reaches equilibrium. At equilibrium, the reaction shown by an equation may be well to the right (mostly new products), well to the left (mostly unchanged reactants) or somewhere in between.

Balance points exist in most reversible reactions where neither the forward nor the reverse reaction is complete. Reactants and products are present together and the reactions appear to have stopped – this is the state of chemical equilibrium.

One way to study the approach to equilibrium is to watch what happens on shaking a small crystal of iodine in a test tube with cyclohexane and a solution of potassium iodide, KI(aq). The liquid cyclohexane and the aqueous solution do not mix.

Iodine freely dissolves in cyclohexane, which is a non-polar solvent (Section 2.7). The non-polar iodine molecules mix with the cyclohexane molecules – there is no reaction. The solution is a purple–violet colour, the same colour as iodine vapour. Iodine hardly dissolves in water but it does dissolve in a solution of potassium iodide. The solution is yellow, orange or brown depending on the concentration. In the solution, iodine molecules, I_2, react with iodide ions, I^-, to form triiodide ions, I_3^-.

Tip

The symbol $\rightleftharpoons$ represents a reversible reaction at equilibrium. In theory it is only possible to achieve a state of equilibrium in a closed system (Section 8.1).

Figure 10.7 is a study of changes which can be summed up by this equilibrium:

$$I_2(\text{in cyclohexane}) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

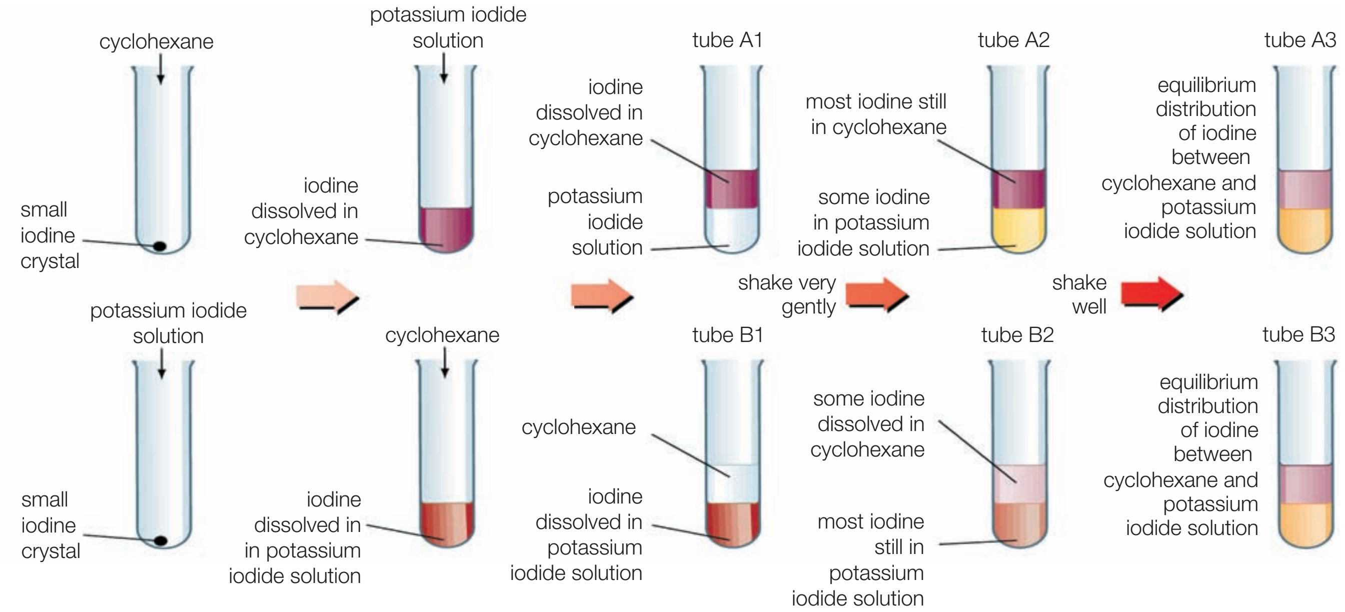

cyclohexane
small iodine crystal
potassium iodide solution
iodine dissolved in cyclohexane
tube A1
iodine dissolved in cyclohexane
potassium iodide solution
shake very gently
tube A2
most iodine still in cyclohexane
some iodine in potassium iodide solution
shake well
tube A3
equilibrium distribution of iodine between cyclohexane and potassium iodide solution
potassium iodide solution
small iodine crystal
cyclohexane
iodine dissolved in in potassium iodide solution
tube B1
cyclohexane
iodine dissolved in potassium iodide solution
tube B2
some iodine dissolved in cyclohexane
most iodine still in potassium iodide solution
tube B3
equilibrium distribution of iodine between cyclohexane and potassium iodide solution

Figure 10.7 Two approaches to the same equilibrium state. Note that the tubes labelled A1, A2 and A3 are the same tube at three different stages. The same is true for the tubes labelled B1, B2 and B3.

The graphs in Figure 10.8 show how the iodine concentration in the two layers changes with shaking. After a little while, no further change seems to take place – tubes A3 and B3 look just the same. Both contain the same equilibrium system.

This demonstration shows two important features of equilibrium processes:

- at equilibrium the concentration of reactants and products does not change
- the same equilibrium state can be reached from either the 'reactant side' or the 'product side' of the equation.

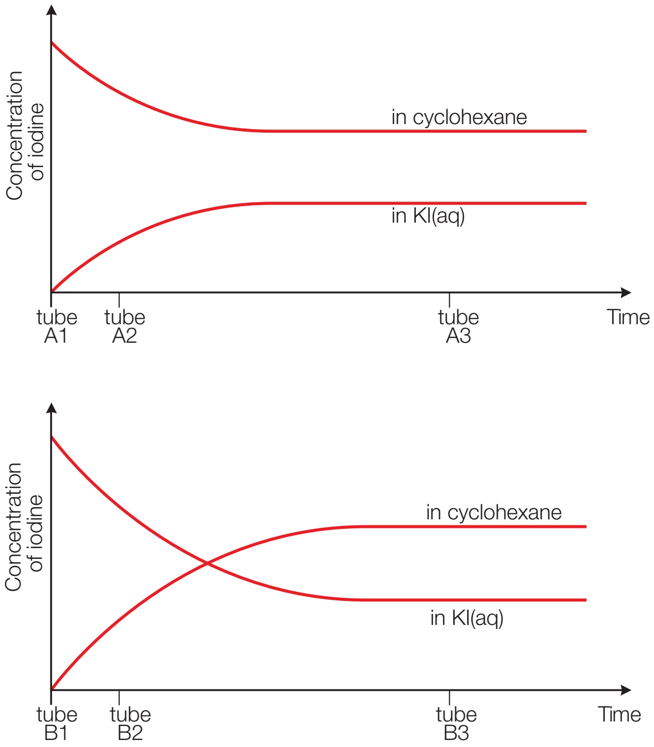


Figure 10.8 Change in concentration of iodine with time in the mixtures shown in Figure 10.7.

10.3 Dynamic equilibrium

Key term

In **dynamic equilibrium**, the forward and backward reactions continue, but at equal rates, so that the overall effect is no change. At the molecular level, there is continuous movement. At the macroscopic level, nothing appears to be happening.

Figure 10.9 shows what is happening at a molecular level – not what your eye can see – in the equilibrium involving iodine moving between cyclohexane and a solution of potassium iodide. Consider tube A1 in Figure 10.7. All the iodine molecules start in the upper cyclohexane layer. On shaking, some move into the aqueous layer. At first, molecules can move in only one direction (the forward reaction). The forward reaction begins to slow down as the concentration in the upper layer falls.

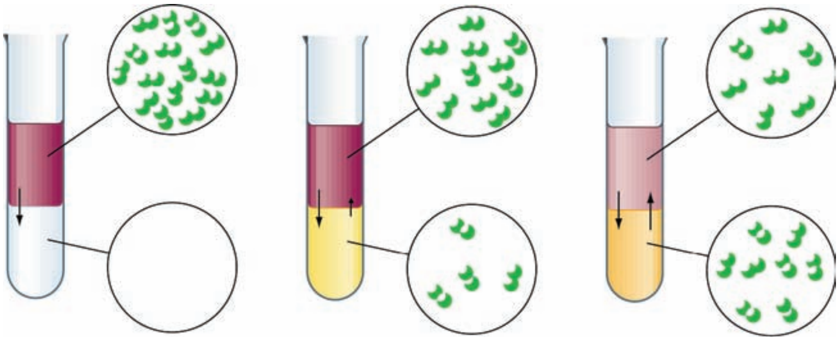


Figure 10.9 Iodine molecules reaching dynamic equilibrium between cyclohexane and a solution of potassium iodide. The formation of I_3^- ions in the aqueous layer is ignored in this diagram.

Once there is some iodine in the aqueous layer, the reverse process can begin with iodine returning to the cyclohexane layer. This backward reaction starts slowly but speeds up as the concentration of iodine in the aqueous layer increases.

In time, both the forward and backward reactions happen at the same rate. Movement of iodine between the two layers continues but overall there is no change. In tube A3 in Figure 10.7 each layer is gaining and losing iodine molecules at the same rate. This is an example of **dynamic equilibrium**.

Test yourself

4 Under what conditions are these in equilibrium:
- **a)** water and ice
- **b)** water and steam
- **c)** copper(II) sulfate crystals and copper(II) sulfate solution?

5 Draw a diagram to represent the movement of particles between a crystal and a saturated solution of the solid in a solvent.

10.4 Factors affecting equilibria

Changing the conditions can disturb a system at equilibrium. At equilibrium the rate of the forward and backward reactions is the same. Anything which changes the rates can shift the balance.

Predicting the direction of change

Le Chatelier's principle is a qualitative guide to the effect of changes in concentration, pressure or temperature on a system at equilibrium. The principle was suggested as a general rule by the French physical chemist Henri Le Chatelier (1850–1936).

The principle states that when the conditions of a system at equilibrium change, the system responds by trying to counteract the change.

Changing the concentration

Table 10.1 shows the effects of changing the concentration in the generalised equilibrium system

$$A + B \rightleftharpoons C + D$$

Table 10.1 Effects of changing the concentration in the generalised equilibrium system.

Disturbance	How does the equilibrium mixture respond?	The result
Concentration of A increases.	System moves to the right – some A is removed by reaction with B.	Less B and more C and D in the new equilibrium.
Concentration of D increases.	System moves to the left – some of the added D is removed by reaction with C.	Less C and more A and B in the new equilibrium.
Concentration of D decreases.	System moves to the right to make up for the loss of D.	There is more C and less A and B in the new equilibrium.

Tip

Note that Le Chatelier's principle is a guide based on lots of observations of reversible processes at equilibrium. The principle does not explain the effect of changing conditions on systems at equilibrium.

The reaction of bromine with water can be used to make predictions based on Le Chatelier's principle. A solution of bromine in water is a yellow–orange colour because it contains bromine molecules in the equilibrium:

$$\underset{\text{orange}}{Br_2(aq)} + H_2O(l) \rightleftharpoons \underset{\text{colourless}}{HOBr(aq)} + Br^-(aq) + H^+(aq)$$

Adding alkali turns the solution almost colourless (Figure 10.10). Hydroxide ions in the alkali react with hydrogen ions, removing them from the equilibrium. As the hydrogen ion concentration falls, the equilibrium shifts to the right, converting orange bromine molecules to colourless molecules and ions. Lowering the hydrogen ion concentration slows down the backward reaction, while the forward reaction goes on as before. The position of equilibrium shifts until, once again, the rates of the forward and backward reactions are the same.

Adding acid increases the concentration of hydrogen ions – this speeds up the backward reaction and makes the solution turn orange–yellow again. The equilibrium shifts to the left reducing the hydrogen ion concentration and increasing the bromine concentration until, once again, the forward and backward reactions are in balance.

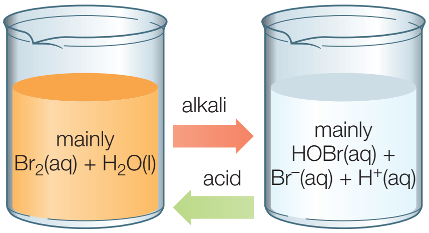


Figure 10.10 The visible effects of adding alkali and acid to a solution of bromine in water.

Test yourself

6 Write an ionic equation for the reversible reaction of silver(I) ions with iron(II) ions to form silver atoms and iron(III) ions. Make a table similar to Table 10.1 to show how Le Chatelier's principle applies to this equilibrium.

7 Yellow chromate(VI) ions, $CrO_4^{2-}(aq)$, react with aqueous hydrogen ions, $H^+(aq)$, to form orange dichromate(VI) ions, $Cr_2O_7^{2-}(aq)$, and water molecules. The reaction is reversible. Write an equation for the system at equilibrium. Predict how the colour of a solution of chromate(VI) ions changes:

- **a)** on adding acid
- **b)** followed by adding hydroxide ions (OH^-), which neutralise hydrogen ions (Section 4.1).

8 Heating limestone, $CaCO_3$, in a closed furnace produces an equilibrium mixture of calcium carbonate with calcium oxide, CaO, and carbon dioxide gas. Heating the solid in an open furnace decomposes the solid completely into the oxide. How do you account for this difference?

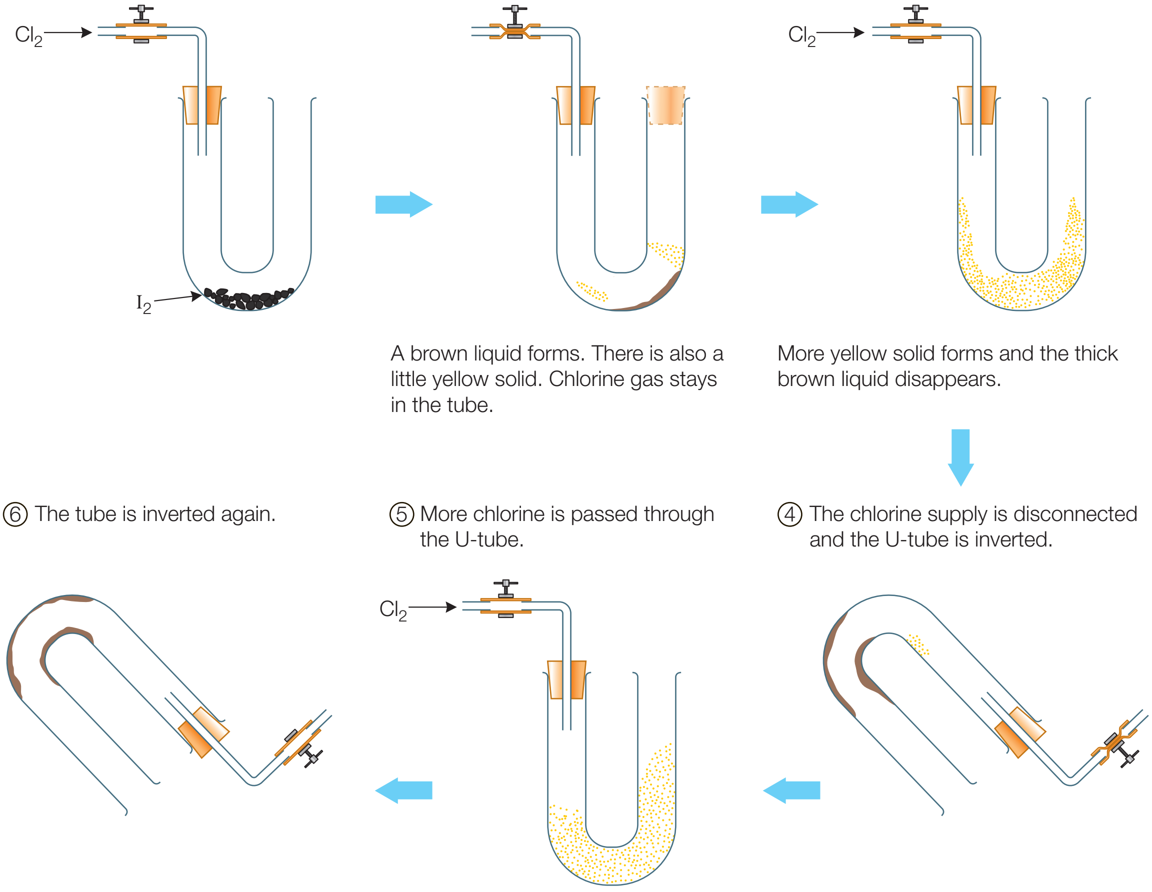
Activity

An equilibrium involving iodine and chlorine

Iodine reacts with chlorine gas to form a brown liquid called iodine monochloride, ICl. Iodine monochloride reacts reversibly with chlorine to form iodine trichloride, ICl_3 which is a yellow solid.

Figure 10.11 shows the steps of a demonstration of these reactions. The steps are outlined above the diagrams. The observations are described below the diagrams.

1. What are the hazards involved in this demonstration and what steps must be taken to reduce the risks?
2. Write an equation, with state symbols, for the reaction that produces the brown liquid.
3. Write an equation, with state symbols, for the reversible reaction of the brown liquid to produce the yellow solid.
4. At what stage in the demonstration is there a dynamic equilibrium between the brown liquid, chlorine and the yellow solid?
5. Explain the conditions under which more of the yellow solid forms.
6. Explain the conditions under which most of the yellow solid disappears.



① Chlorine is passed over iodine crystals.

② The chlorine supply is stopped and the U-tube stoppered.

A brown liquid forms. There is also a little yellow solid. Chlorine gas stays in the tube.

③ More chlorine is passed through the U-tube.

More yellow solid forms and the thick brown liquid disappears.

④ The chlorine supply is disconnected and the U-tube is inverted.

Chlorine gas ‘falls out’ of the tube. The brown liquid reappears as the yellow solid disappears.

⑤ More chlorine is passed through the U-tube.

The yellow solid reappears as the thick brown liquid disappears.

⑥ The tube is inverted again.

The brown liquid reappears as the yellow solid disappears.

Figure 10.11 A demonstration to show how changing conditions can alter the position of an equilibrium.

Changing the pressure and temperature

Many industrial processes happen in the gas phase. High pressures and high temperatures are often needed, even when there is a catalyst. One important example of this is the Haber process used to make ammonia. The equilibrium system involved is:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4\,\text{kJ}\,\text{mol}^{-1}$$

The reaction takes place in a reactor packed with an iron catalyst. Adding a catalyst does not affect the position of equilibrium. A catalyst simply speeds up both the forward and the back reactions by the same amount, so it shortens the time taken to reach equilibrium.

Le Chatelier's principle helps to explain the conditions chosen for the Haber process. There are 4 mol of gases on the left-hand side of the equation but only 2 mol on the right. Increasing the pressure makes the equilibrium shift from left to right, because this reduces the number of molecules and tends to reduce the pressure. So, increasing the pressure increases the proportion of ammonia at equilibrium.

The reaction is exothermic from left to right and, therefore, endothermic from right to left. Le Chatelier's principle predicts that raising the temperature makes the system shift in the endothermic direction which takes in energy (tending to lower the temperature). So, raising the temperature lowers the proportion of ammonia at equilibrium.

In industry, the conditions chosen are a compromise between the need to convert as much nitrogen and hydrogen to ammonia as possible in the reactor (high pressure and low temperature) and the need to produce ammonia fast enough (high pressure, high temperature and the presence of a catalyst).

In practice, a wide range of conditions are used, depending on the design of the reactor. The temperatures used vary from 600 to 700 K. Pressures range from 50 to 100 times atmospheric pressure.

Test yourself

9 Explain why the conditions used in the industrial Haber process are a compromise.

10 Methanol is manufactured from carbon dioxide and hydrogen in the presence of a catalyst that consists of a mixture of copper and zinc oxides coated onto pellets of aluminium oxide. For this reaction $\Delta H^{\ominus} = -91\,\text{kJ}\,\text{mol}^{-1}$.

  a) Write a balanced equation for the reaction.

  b) Suggest a reason for coating the catalyst onto the surface of pellets on an inert material.

  c) Suggest reasons why the process is carried out at 550 K and 100 times atmospheric pressure.

Activity

The manufacture of ethanol

Ethanol is manufactured from ethene and steam in the presence of a catalyst.

$$C_2H_4\,(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \quad \Delta H = -45\,\text{kJ}\,\text{mol}^{-1}$$

The catalyst in the reactor is phosphoric acid held as a thin film coating the surface of finely divided solid silicon dioxide. The catalyst absorbs water under pressure. This dilutes the catalyst and may lead to it draining away from the solid support.

The process is carried out at about 500 K with a pressure in the range 60–70 times atmospheric pressure. If the pressure is too high, the ethene starts to polymerise.

Only about 5% of the ethene is converted to ethanol as the mixture of reactants passes through the reactor. The product is condensed from the gases leaving the reactor. At this stage the ethanol formed contains a high proportion of water.

1 What is the main source of ethene for industrial processes?

2 The ratio of water : ethene supplied to the reactor is 0.6 mol : 1 mol. Suggest the factors that determine this ratio.

3 Suggest the factors that determine the choice of 500 K as the operating temperature for the process.

4 Suggest the factors that determine the choice of 60–70 times atmospheric pressure as the operating pressure for the process.

5 In practice, the process converts 95% of the ethene to ethanol. Suggest how this is achieved.

6 Suggest the method that is used to concentrate the ethanol produced in the process.

10.5 Equilibrium constants

Chemists have discovered a law that can be used to predict the amounts of reactants and products when a reversible reaction reaches a state of dynamic equilibrium. The equilibrium law has been established by experiment. It is a quantitative law for predicting the amounts of reactants and products present when a reaction reaches a state of dynamic equilibrium.

In general, for a reversible reaction at equilibrium:

$$aA + bB \rightleftharpoons cC + dD \qquad K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Key term

A shorthand for **concentration** in mol dm^{-3} is to write the formula of a chemical in square brackets. For example: [A] represents the concentration of A in mol dm^{-3}.

This is the form for the equilibrium constant, K_c, when the **concentrations** of the reactants and products are measured in moles per cubic decimetre. [A], [B] and so on are the equilibrium concentrations, sometimes written as $[A]_{eqm}$ and $[B]_{eqm}$ to make this clear.

The concentrations of the chemicals on the right-hand side of the equation appear on the top line of the expression. The concentrations of reactants on the left appear on the bottom line. Each concentration term is raised to the power of the number in front of its formula in the equation.

Tip

In your AS course you only have to be able to write the expression for K_c based on the balanced equation for the reversible reaction. You will learn to apply the equilibrium law quantitatively in the second part of your A Level course.

Equilibrium constants and balanced equations

An equilibrium constant always applies to a particular chemical equation and can be deduced directly from the equation.

There are two common ways of writing the reaction of sulfur dioxide with oxygen. As a result, there are two forms for the equilibrium constant, which have different values. So long as the matching equation and equilibrium constant are used, the predictions based on the equilibrium law are the same.

For:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \text{Equation 1}$$

$$K_c = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$$

But for:

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \qquad \text{Equation 2}$$

$$K_c = \frac{[SO_3(g)]}{[SO_2(g)][O_2(g)]^{1/2}}$$

So it is important to write the balanced equation and the equilibrium constant together.

Reversing the equation also changes the form of the equilibrium constant because the concentration terms for the chemicals on the right-hand side of the equation always appear on the top of the expression for K_c.

So for:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad \text{Equation 3}$$

$$K_c = \frac{[SO_2(g)]^2[O_2(g)]}{[SO_3(g)]^2}$$

Test yourself

11 Write the balanced equation and the expression for K_c for these reversible reactions:

a) hydrogen gas with iodine gas to form hydrogen iodide gas

b) nitrogen monoxide gas with oxygen gas to form nitrogen dioxide gas

c) nitrogen gas with hydrogen gas to form ammonia gas.

Heterogeneous equilibria

In an equilibrium mixture of sulfur dioxide, oxygen and sulfur trioxide all three substances are gases. They are all in the same gaseous phase. This is an example of a **homogeneous equilibrium**.

In many equilibrium systems the substances involved are not all in the same phase. An example is the equilibrium state involving two solids and a gas formed on heating calcium carbonate in a closed container. In this system there are two solid phases and a gas phase. This is an example of a **heterogeneous equilibrium**.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The concentrations of solids do not appear in the expression for the equilibrium constant. Pure solids have, in effect, a constant 'concentration'. So $K_c = [CO_2(g)]$

The same applies to heterogeneous systems which have a separate pure liquid phase as one of the reactants or products.

Key terms

A **homogeneous equilibrium** is an equilibrium in which all the substances involved are in the same phase.

A **heterogeneous equilibrium** is an equilibrium system in which the substances involved are in more than one phase.

Test yourself

12 Write the expression for K_c for these equilibria:

a) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

b) $H_2(g) + S(l) \rightleftharpoons H_2S(g)$

c) $Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$

13 Write the balanced equations for the equilibria to which these expressions for K_c apply:

a) $K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$

b) $K_c = \frac{[H_2(g)][CO_2(g)]}{[H_2O(g)][CO(g)]}$

c) $K_c = \frac{[Cr^{2+}(aq)]^2[Fe^{2+}(aq)]}{[Cr^{3+}(aq)]^2}$

Qualitative predictions based on the equilibrium law

The equilibrium law makes it possible to explain qualitatively the effect of changing the concentration of one of the chemicals in an equilibrium mixture. This is an alternative approach to applying Le Chatelier's principle.

An example is the equilibrium in an aqueous solution of bromine (Section 10.4):

$$Br_2(aq) + H_2O(l) \rightleftharpoons HOBr(aq) + Br^-(aq) + H^+(aq)$$

At equilibrium:

$$K_c = \frac{[HOBr(aq)][Br^-(aq)][H^+(aq)]}{[Br_2(aq)]}$$

where these are equilibrium concentrations.

Adding a few drops of alkali neutralises $H^+(aq)$ on the right-hand side of the equation. This reduces the value of $[H^+(aq)]$ and briefly upsets the equilibrium so that for an instant after adding alkali:

$$K_c > \frac{[HOBr(aq)][Br^-(aq)][H^+(aq)]}{[Br_2(aq)]}$$

The system restores equilibrium as the forward reaction predominates and bromine molecules react with water to produce more of the products. There is very soon a new equilibrium. Once again:

$$\frac{[HOBr(aq)][Br^-(aq)][H^+(aq)]}{[Br_2(aq)]} = K_c$$

but now with new values for the various equilibrium concentrations.

Chemists sometimes say that adding alkali makes the 'position of equilibrium shift to the right'. The effect is visible because the orange colour of the bromine molecules fades with the formation of more colourless molecules and ions on the right-hand side of the equation. This is as Le Chatelier's principle predicts (Section 10.4). The advantage of using K_c is that it makes quantitative predictions possible.

Tip

In dilute solution, the water is in such large excess that the value of $[H_2O(l)]$ is effectively constant. As a result, it does not appear in the equilibrium law expression.

Tip

Changing the concentrations does not alter the value of the equilibrium constant so long as the temperature stays constant.

Test yourself

14 Calculate the concentration of water in water (in $mol\,dm^{-3}$) to show that it is reasonable to regard the concentration of water as a constant when writing the expression for K_c for equilibria in dilute aqueous solution.

Exam practice questions

1 Carbon dioxide is dissolved in water under pressure to make sparkling mineral water. In a bottle of mineral water, there is an equilibrium between carbon dioxide dissolved in the drink, $CO_2(aq)$, and carbon dioxide in the gas above the drink, $CO_2(g)$.

a) Write an equation to represent the equilibrium between carbon dioxide gas and carbon dioxide in solution. *(1)*

b) Use this example to explain the term 'dynamic equilibrium'. *(2)*

c) Explain why lots of bubbles of gas form when a bottle of sparkling mineral water is opened. *(2)*

d) Less than 1% of the dissolved carbon dioxide reacts with water. It forms hydrogencarbonate ions:

$$CO_2(g) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

Use this equation to explain why carbon dioxide is much more soluble in sodium hydroxide solution than in water. *(2)*

● **2** Haemoglobin is a large molecule in red blood cells that can be represented by the symbol Hb. Haemoglobin carries oxygen in the blood from our lungs to the cells in our bodies:

$$\text{Hb(aq)} + 4\text{O}_2\text{(g)} \rightleftharpoons \text{HbO}_8\text{(aq)}$$

a) Suggest a reason why haemoglobin takes up oxygen as blood passes through the blood vessels in the lungs. *(2)*

b) Suggest a reason why haemoglobin releases oxygen as blood passes through the blood vessels between cells in muscles. *(2)*

c) Haemoglobin molecules are affected by the presence of carbon dioxide. The molecules hold onto oxygen less strongly if the carbon dioxide concentration is higher. Why does this help the blood deliver oxygen to cells in muscles? *(2)*

● **3** For each of the following equilibria predict the effects, if any, of:

i) raising the pressure

ii) raising the temperature.

a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ *(3)*

This reaction is slightly exothermic.

b) $NaCl(s) + aq \rightleftharpoons NaCl(aq)$ *(3)*

The enthalpy change of solution of NaCl is slightly positive and there is a slight decrease in volume when salt dissolves in water.

c) $C(graphite) \rightleftharpoons C(diamond)$

$\Delta H = +1.9\,\text{kJ mol}^{-1}$ *(4)*

The density of diamond is $3.5\,\text{g cm}^{-3}$. The density of graphite is $2.3\,\text{g cm}^{-3}$.

● **4 a)** Explain why iodine is much more soluble in aqueous potassium iodide solution than in water. *(3)*

b) A solution of iodine in KI(aq) is dark yellow-brown. Explain why, on adding sodium thiosulfate solution, the solution gradually loses its colour, turning paler and paler yellow until finally becoming colourless. *(5)*

● **5** Sulfuric acid is manufactured by the contact process which involves the reversible reaction of sulfur dioxide with oxygen from the air to form sulfur trioxide. For this reaction $\Delta H = -198\,\text{kJ mol}^{-1}$. The reaction takes place in the presence of a vanadium(v) oxide catalyst which does not work unless it is hot.

a) Write a balanced equation for the reaction involved in the contact process. *(1)*

b) In theory, what conditions favour the maximum conversion of sulfur dioxide to sulfur trioxide in the reactor? *(6)*

c) A mixture of sulfur dioxide and air is fed into the reactor. Suggest a reason why equal amounts of sulfur dioxide and oxygen are present in the mixture fed into the reactor. *(3)*

d) Suggest reasons for the fact that, in practice, the process is carried out at 700 K and at atmospheric pressure. *(6)*

● **6** Write equations and the expressions for K_c for these reversible reactions:

a) the reaction of hydrogen with chlorine to make hydrogen chloride. *(3)*

b) the reaction of ammonia with oxygen to form nitrogen monoxide and steam. *(3)*

c) the decomposition of solid NH_4HS to ammonia gas and hydrogen sulfide gas. *(3)*

● **7** Hydrogen is manufactured from methane and steam. In the first stage of the process, methane is mixed with a large excess of steam and passed through a reactor containing a nickel catalyst. The reversible reaction produces carbon monoxide and hydrogen. For this reaction $\Delta H = +210\,\text{kJ mol}^{-1}$.

In the second part of the process, the carbon monoxide gas reacts with steam to form carbon dioxide and more hydrogen. At 700 K the equilibrium constant for this reaction $K_c = 5.1$. At 1100 °C the value of $K_c = 1.0$.

Finally, the carbon dioxide is removed from the gas mixture using a molecular sieve made of a zeolite.

a) What conditions favour the formation of products in the first part of the process? Explain your answer. *(6)*

b) i) Write the equation and expression for K_c for the reaction used in the second stage of the process. *(2)*

ii) Use the two values of K_c to determine whether the reaction is exothermic or endothermic, giving your reasons. *(3)*

iii) Suggest reasons why the reaction is carried out at 650 K in the presence of an iron catalyst. *(2)*

c) Explain why zeolites can be used as molecular sieves. *(2)*

d) Suggest reasons why the carbon dioxide made in this process is captured and stored. *(3)*

e) Explain why hydrogen is manufactured on a large scale. *(2)*

A1

Mathematics in (AS) chemistry

In order to be able to develop your skills, knowledge and understanding in chemistry, you need to be competent in certain areas of mathematics. At least 20% of the marks in your examinations will require the use of mathematical skills at the standard of higher tier GCSE mathematics, but applied in the context of A Level chemistry.

A1.1 Mathematical operations

Mathematics uses the term *operations* to describe processes such as addition, subtraction, multiplication, division and squaring. Certain rules apply to the order in which these operations are carried out, irrespective of the order in which they are written on the page. The most important rule is that multiplication is always done *before* addition. For example, the correct answer to the calculation $7 + 2 \times 3$ is 13 because the multiplication 2×3 is done first and then the product, 6, is added to 7 to give 13.

This calculation could perhaps have been written more clearly using brackets as $7 + (2 \times 3) = 13$. This shows that the calculation inside a bracket is done first, before any multiplication or addition outside the brackets.

The order of operations is important, for instance, in the calculation of relative molar masses.

Example

Calculate the M_r of aluminium sulfate, $Al_2(SO_4)_3$.

Notes on the method

The M_r is the sum of the A_r for the atoms in the formula, with the multiplications done before the additions.

Answer

$$M_r[Al_2(SO_4)_3] = 2 \times A_r(Al) + 3 \times [A_r(S) + 4 \times A_r(O)]$$

The M_r of SO_4 inside the bracket in the chemical formula is found first.

$$\begin{aligned} M_r(SO_4) &= A_r(S) + 4 \times A_r(O) \\ &= 32.1 + 4 \times 16.0 \\ &= 32.1 + 64.0 \qquad \text{(multiplication before division)} \\ &= 96.1 \end{aligned}$$

Tip

The relative atomic masses in the periodic table in the Edexcel Data booklet are given to one decimal place. You should use the figures for A_r to this precision in your calculations.

Then multiplication of the M_r of SO_4 by the number 3 outside the bracket in the chemical formula gives:

$$\begin{aligned} M_r[(SO_4)_3] &= 3 \times M_r(SO_4) \\ &= 3 \times 96.1 \\ &= 288.3 \end{aligned}$$

$A_r(Al) = 27.0$ so $2 \times A_r(Al) = 54.0$

Final addition gives:

$$\begin{aligned} M_r[Al_2(SO_4)_3] &= 2 \times A_r(Al) + M_r[(SO_4)_3] \\ &= 54.0 + 288.3 = 342.3 \end{aligned}$$

A1.2 Positive and negative numbers

Chemists use oxidation numbers (Section 3.3) to represent the numbers of electrons gained or lost by an atom. Oxidation numbers can be positive or negative. The oxidation number of chlorine in the chloride ion is –1 and of oxygen in the oxide ion is –2.

Beware of describing the oxidation number of oxygen as 'bigger' than that of chlorine in these two ions. The comparisons bigger/smaller and higher/lower are unclear when discussing negative numbers. You should always make it totally clear what you mean, so you should say that the oxidation number of oxygen in the oxide ion is *more negative* than that of chlorine in chloride.

Similar care is needed when discussing exothermic reactions where heat energy is evolved and the enthalpy change, ΔH is negative (Section 8.2). For methane, the standard enthalpy of combustion, $\Delta H^{\ominus} = -890\,\text{kJ mol}^{-1}$ and for ethane, the standard enthalpy of combustion, $\Delta H^{\ominus} = -1560\,\text{kJ mol}^{-1}$. Take care to say that the value for ethane is *more negative* than that for methane, not just bigger.

Tip

Take care when using negative numbers, for instance in calculations using Hess's Law (Section 8.5) or bond energies (Section 8.7). Use brackets around negative numbers and remember that $x - (-y) = x + y$.

A1.3 Standard form and ordinary form

Numbers in chemistry vary from the extremely large, such as the Avogadro constant (Section 5.1), to the extremely small, such as the mass of a proton in kilograms. A convenient way to write both numbers is called **standard form**. This avoids the long strings of zeros which would be needed if the number were written in **ordinary form**.

In standard form, a number is written in two parts which are multiplied together, $a \times 10^b$.

The number a is greater than 1 and less than 10, and b is a whole number.

If the overall number < 1, then b is a negative number.

If the overall number > 10, then b is a positive number.

Key terms

Standard form writes a number in two parts multiplied together. The first part is a number greater than 1 and less than 10; the second part is the number 10 raised to a power which is a whole number.

In **ordinary form** a number is written with no powers of ten included.

Tip

The statement 'a is greater than 1 and less than 10' can be represented mathematically as $1 < a < 10$, where the symbol $<$ means 'is less than'. Similarly the symbol $>$ means 'is greater than' and the symbol $>>$ means 'is very much greater than'.

Tip

The value of *b* gives the number of places that the decimal point must be moved when changing between ordinary form and standard form.

Tip

Always use standard form if possible; it reduces the chance of error when counting numbers of zeros.

Examples of standard form

The number 0.002 46 in ordinary form becomes 2.46×10^{-3} when expressed in standard form. The decimal point is moved three places to the right.

The number 135 000.0 in ordinary form becomes 1.35×10^{5} when expressed in standard form. The decimal point is moved five places to the left.

The Avogadro constant (Section 5.1) in standard form is 6.02×10^{23} mol^{-1}.

This is much more convenient to use than the ordinary form, which is 602 000 000 000 000 000 000 000 mol^{-1}.

The mass of a proton expressed in standard form is 1.67×10^{-27} kg.

This is much easier to use than the ordinary form, which is 0.000 000 000 000 000 000 000 000 001 67 kg.

When adding or subtracting numbers written in standard form, make sure that the addition or subtraction is done on equivalent numbers in which the powers of ten are the same.

Example

A solution containing 1.60×10^{-2} mol HCl is added to a solution containing 4.50×10^{-3} mol HCl.

Calculate the total amount in moles of HCl present.

Answer

In order to convert both numbers to the same powers of ten we can rewrite 4.50×10^{-3} as 0.450×10^{-2}

The addition is then $(1.60 + 0.450) \times 10^{-2} = 2.05 \times 10^{-2}$

When multiplying numbers in standard form, the powers are added together, as is usual with indices, so $10^2 \times 10^3 = 10^5$.

Example

Calculate the amount in moles of solute in 250 cm^3 of a 0.0130 mol dm^{-3} solution.

Answer

The amount of solute (in moles) in a solution is given by multiplying the volume in dm^3 by the concentration in mol dm^{-3} (Section 5.5).

Volume = 250 cm^3 = 2.50×10^{-1} dm^3

Concentration = 0.0130 mol dm^{-3} = 1.30×10^{-2} mol dm^{-3}

$$\begin{aligned}\text{Amount of solute} &= (2.50 \times 10^{-1}) \times (1.30 \times 10^{-2})\\ &= (2.50 \times 1.30) \times 10^{-(1+2)}\\ &= 3.25 \times 10^{-3}\ \text{mol}\end{aligned}$$

A1.4 Handling data

Significant figures

When writing numbers, it is important to give a suitable number of digits. The number of written digits is called the number of significant figures, often abbreviated to sig. figs or s.f. For example, 6.8 g has 2 significant figures, whereas 6.84 g has 3 significant figures.

Zeros to the left of a number are ignored, and the number of significant figures is determined starting with the leftmost non-zero digit. So 0.0506 has 3 significant figures. This is more obvious if the number is written in standard form as 5.06×10^{-2}.

Zeros to the right of a number are significant, so 3.740 has 4 significant figures.

When a measurement is made, it is important to know how precise that measurement is (Section 5.9) and, therefore, what is an appropriate number of significant figures to give. A titre might be given as 25.65 cm^3, that is to 4 significant figures, but a time might only be given as 23 seconds (to 2 s.f.).

A value can be rounded to a smaller number of significant figures but should never be written to a greater number of significant figures than could be measured with the equipment used.

So a volume of 25.65 cm^3 (4 s.f.) measured using a burette might be rounded to 25.7 cm^3 (3 s.f.) but a volume of 26 cm^3 measured using a measuring cylinder with 2 cm^3 divisions should never be given to more than 2 significant figures.

Tip

Rounding means replacing a number containing lots of digits with an approximate, but shorter and more convenient, number.

When rounding to 3 significant figures, look at the fourth figure. If is it 5 or more, you should round the third figure up. If the fourth figure is 4 or less, do not round up. So you should round 123.4 to 123 (3 s.f.), but 234.5 rounds to 235 (3 s.f.). Therefore, the number 123 (to 3 s.f.) is the approximation which represents values with 4 significant figures between 122.5 and 123.4.

In a calculation, the number with the fewest significant figures determines the number of significant figures in the answer. So, if a number with 4 significant figures is multiplied by one with only 2 significant figures, the result should only be quoted to 2 significant figures.

Some experiments contain many sources of error, for instance the energy losses in combustion experiments. Results from such experiments should not be quoted to more than 2 or 3 significant figures (Section 8.3).

Tip

Sometimes rounding numbers allows you to estimate what the answer to a calculation *should* be. Then, if your calculator produces a very different result, you know you have made a mistake. For instance, you know that the answer of 4.95 × 2.12 should be approximately 5 × 2 = 10.

In calculations with several steps it is better not to use your calculator at each stage. The danger is that you round the answer of each step and introduce 'rounding errors'. You will get a more accurate answer if you use your calculator once at the end to work out the answer, and only round to the correct number of significant figures in this final answer.

Tip

If you do need to use your calculator at stages during a problem and the final answer is required to 3 significant figures, work in 4 or 5 significant figures during the earlier stages and only round your answer to 3 significant figures at the very end.

Units and decimal places

Unlike pure numbers, a physical quantity includes both the number value and its units, so a mass may be 5.0 g, a volume 25.0 cm^3 and a molar mass 98.1 $g\,mol^{-1}$. The number value depends on the units and it is often sensible to change, for instance, from one volume unit to another to simplify a number. So a volume of 0.0035 dm^3 of solution with several decimal places may be more conveniently written as 3.5 cm^3 (or of course in standard form as $3.5 \times 10^{-3}\,cm^3$). (See also the combustion example in Section 8.3, where an energy change in joules is changed into kJ to simplify the numbers.)

Tip

In calculations, using numbers with their units leads directly to an answer with its correct units. This is good practice as not only does this produce the correct units easily but also acts as a check on the calculation.

The number of decimal places given in a measurement also depends on the equipment used. A three decimal place balance will allow measurements such as 3.456 g to be made.

However, the number of decimal places is much less important than the number of significant figures. You may think that a figure of 0.005 g looks impressively precise as it is given to 3 decimal places (precision is discussed in Section 5.9). But 0.005 g is only given to 1 significant figure (and can mean anything between 0.0045 and 0.0054 g), so it is less precise than a figure such as 2.5 g which, although only given to 1 decimal place, is to 2 significant figures.

Key terms

The **arithmetic mean** of a list of numbers is the total value of the list divided by the size of the list.

Outliers are experimental results which lie well away from the others.

Arithmetic means

One way a series of numbers can be compared is by taking their average. This usually means adding the series of numbers together and dividing by size of the series. This 'average' is strictly called an **arithmetic mean**.

Tip

In statistics, average can also mean the median or the mode. These terms are not needed in chemistry at this level of study.

Most experiments are repeated to check for anomalous results, that is for results that lie away from the others. These results are sometimes called **outliers** and may be due to experimental error. Once these anomalous results are identified, the arithmetic mean can be calculated from the rest of the data without these outliers.

Every volumetric analysis involves an initial rough titration which is used to get an idea of the volume needed. Thereafter, the end-point can be approached slowly, so that further titrations, if done carefully, should lead to concordant results. Any result which is not concordant is ignored and the average volume added, the arithmetic mean, is calculated by adding the titres together and dividing this total by the number of results.

Example

Table A1.1 shows a set of titration results. Use the concordant titres from the table to calculate a mean titre.

Answer

Titre 2 is not concordant. It is not within 0.10 cm^3 of the others and is ignored. It is an outlier.

The other three titres are concordant and their total

$$= 23.40 + 23.30 + 23.35 = 70.05\,\text{cm}^3$$

The arithmetic mean of these three results $= \dfrac{70.05\,\text{cm}^3}{3} = 23.35\,\text{cm}^3$

Table A1.1 Titration results.

	Rough	Accurate 1	Accurate 2	Accurate 3	Accurate 4
Final burette reading	26.5	27.00	25.75	25.90	26.45
Initial burette reading	2.0	3.60	2.15	2.60	3.10
Titre/cm^3	24.5	23.40	23.60	23.30	23.35
Used in calculation		✓	✗	✓	✓

Weighted means

Another example of the need to find an arithmetic mean occurs in the calculation of the relative atomic mass of an element using isotopic abundances (see the example in Section 1.4).

Examples of this type, however, do not use a simple arithmetic mean but a **weighted mean**.

A simple arithmetic mean of the relative atomic masses of the two chlorine isotopes, chlorine-35 and chlorine-37 would be 36. But, on average, there are 3 atoms of chlorine-35 to every 1 atom of chlorine-37, so these proportions must be taken into account.

The relative atomic mass of chorine is, therefore, a weighted mean given by

$$\frac{\text{total mass of 3 atoms of }^{35}\text{Cl and 1 atom of }^{37}\text{Cl}}{\text{the total number of atoms}} = \frac{(3 \times 35) + (1 \times 37)}{4}$$

$$= 35.5$$

Weighted means can also be calculated using **percentage** abundances for the isotopes (see the example in Section 1.4 using the percentage abundance of the magnesium isotopes).

Key terms

A **weighted mean** is an arithmetic mean of a set of numbers in which some of the numbers carry more importance or weight than others.

Percentage (symbol %) means 'out of 100'. A fraction can be converted into a percentage simply by multiplying by 100, so $\frac{1}{2}$ as a percentage is $(\frac{1}{2} \times 100) = 50\%$.

Tip

Remember that relative atomic masses do not have units because they are ratios (see Section 1.4).

Ratios

In the calculation of the relative atomic mass of chlorine above, the **ratio** of ^{35}Cl atoms to ^{37}Cl is 3 : 1.

The **proportion** of ^{35}Cl is $\frac{3}{4}$ or 75% of the total number of chlorine atoms.

Key terms

A **ratio** is the comparison of two numbers.

Proportion is the ratio of a part compared to the whole amount.

The formula used to describe a molecular substance, the molecular formula, shows the actual number of atoms of each element in one molecule. The formula of an ionic substance, however, is an empirical formula and shows only the ratio of each of the ions present in the giant lattice. The empirical formula is calculated from experiments which measure the mass of each element in a compound. These masses are converted to amounts in moles and then the simplest ratio of these amounts found (see the examples in Sections 5.2 and 6.1.3).

A1.5 Mathematical equations and expressions

Chemists use mathematical equations and expressions in calculations.

For instance, the amount in moles can be expressed in three ways:

- using masses

$$\text{amount/mol} = \frac{\text{mass/g}}{\text{molar mass/g mol}^{-1}}$$

- using gas volumes

$$\text{amount of gas/mol} = \frac{\text{volume/cm}^3}{\text{molar volume/cm}^3\,\text{mol}^{-1}}$$

- using solutions

$$\text{amount of solute/mol} = \frac{\text{volume of solution/dm}^3 \times \text{concentration}}{\text{mol dm}^{-3}}$$

It is important to note that these quantities are combined with their units.

The left-hand side of each expression gives the amount in moles.

Therefore, the units on the right-hand side of each expression should cancel to give mol.

For the mass expression, the 'g' cancels and $\frac{1}{\text{mol}^{-1}} = \text{mol}$

For the volume expression, the 'cm^3' cancels and $\frac{1}{\text{mol}^{-1}} = \text{mol}$

For the solution expression, dm^3 multiplied by dm^{-3} cancels leaving mol.

Tip

10^{-1} means $\frac{1}{10}$ or 0.1 and $\frac{1}{10^{-1}}$ means 10.

(Check: $10^{-1} = 0.1$, so $\frac{1}{10^{-1}} = \frac{1}{0.1} = 10$; correct.)

Similarly, mol^{-1} means $\frac{1}{\text{mol}}$ and dm^{-3} means $\frac{1}{\text{dm}^3}$.

Therefore $\frac{1}{\text{mol}^{-1}}$ means mol and $\frac{1}{\text{dm}^{-3}}$ means dm^3.

One commonly required mathematical skill is to change the subject of an equation. This involves rearrangement of the terms in a mathematical equation to leave the required term alone on one side. Values are then substituted into the rearranged expression.

Example

0.258 mol of a compound has a mass of 46.3 g. Calculate the molar mass of the compound.

Notes on the method

In order to calculate the molar mass of a substance, we start with the expression which includes it:

$$\text{amount/mol} = \frac{\text{mass/g}}{\text{molar mass/g mol}^{-1}}$$

The molar mass, which is the denominator (the underneath) of the fraction, needs to become the subject of a new expression. (It needs to be on the left-hand side of the equation on its own.)

This can be done in stages, as shown below, and then the values given in the question can be substituted into the rearranged expression.

Answer

Start by multiplying both sides of the original equation by molar mass/g mol^{-1}

$$\text{amount/mol} \times \text{molar mass/g mol}^{-1} = \frac{\text{mass/g}}{\text{molar mass/g mol}^{-1}} \times \text{molar mass/g mol}^{-1}$$

The right-hand side cancels to give mass/g, so the overall equation becomes:

$$\text{amount/mol} \times \text{molar mass/g mol}^{-1} = \text{mass/g}$$

Then both sides of the equation are divided by amount/mol giving:

$$\frac{\text{amount/mol}}{\text{amount/mol}} \times \text{molar mass/g mol}^{-1} = \frac{\text{mass/g}}{\text{amount/mol}}$$

Which simplifies to give the required equation:

$$\text{molar mass/g mol}^{-1} = \frac{\text{mass/g}}{\text{amount/mol}}$$

Substituting the numerical values into the equation gives:

$$\begin{aligned}\text{molar mass/g mol}^{-1} &= \frac{46.3\,\text{g}}{0.258\,\text{mol}}\\ &= 179.5\,\text{g mol}^{-1}\\ &= 180\,\text{g mol}^{-1}\ (3\ \text{s.f.})\end{aligned}$$

So the molar mass of the compound is 180 g mol^{-1} .

Tip

Include the units at every stage.

(See also Section 5.5 and the rearrangement of the formula in the example in Section 5.6.)

A1.6 Chemical equations

Chemical equations are often called the language of chemistry. They translate information about types and amounts of substances into a shorthand using symbols and formulae.

A chemical equation shows the substances present at the start of a reaction (the reactants, which are always on the left-hand side), the substances present at the end of a reaction (the products, which are always on the right-hand side) and the mole ratio of all the substances involved in the reaction.

Chemical equations are always balanced, so that the number and type of each element is equal on both sides of the equation and, therefore, the total mass on each side of the equation is equal. The mass is, however, present in different species, as elements or compounds, on the two sides of the equation.

The formulae of the species and the mole ratios allow chemists to calculate the amounts of substances used and formed in reactions.

Calculations involving masses

The four key steps for solving problems using equations were set out in Section 5.4.

Tip

Make sure you can write correct formulae!

Step 1: Write the balanced equation for the reaction.

If the formulae of the substances in the equation are wrong, the equation cannot be balanced and the calculation will be wrong.

Step 2: Write down the amounts in moles of the relevant reactants and products in the equation.

If the equation isn't balanced, the mole ratio will be wrong and the calculation will be wrong.

Step 3: Convert these amounts in moles of the relevant reactants and products to masses.

Work out the molar mass first, then multiply your answer by the ratio from the equation.

Step 4: Scale the masses to the quantities required.

Example

This example uses the data in the first example in Section 5.4, which showed how to calculate the amount of iron that can be obtained from 1.0 kg of iron ore.

What mass of carbon dioxide is also formed?

Answer

Step 1: From the example in Section 5.4, the equation for the reaction is:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

Step 2: The mol ratio of Fe_2O_3 to CO_2 = 1 : 3

Step 3: Work out the M_r of CO_2 (44.0 g mol^{-1}).
Then multiply the answer by the ratio in the equation (1 : 3).
So, starting from 1 mol of Fe_2O_3,
the mass of CO_2 formed = 3 × 44.0 = 132.0 g
(Don't work out the mass of 3C then $3O_2$.)

Step 4: Scale the masses to the quantities required.
M_r of Fe_2O_3 is 159.6 g mol^{-1}

So, starting from 1.0 g Fe_2O_3,

$$\text{the mass of } CO_2 \text{ formed} = \frac{1.0}{159.6} \times 132.0$$
$$= 0.827\,g = 0.83\,g \text{ (2 s.f.)}$$

So for 1 kg of iron ore, the mass of carbon dioxide formed is 830 g.

Calculations using gas volumes

Gas volume calculations are straightforward when all the relevant substances are gases, because the ratio of the gas volumes in the reaction is the same as the ratio of the numbers of moles in the equation (Section 5.4).

If a question involves both masses and gas volumes, then use is made of the first two expressions in Section A1.4 above.

The amount in moles of a solid can be found using the expression:

$$\text{amount/mol} = \frac{\text{mass/g}}{\text{molar mass/g mol}^{-1}}$$

The amount in moles of a gas can be found using the expression:

$$\text{amount of gas/mol} = \frac{\text{volume/cm}^3}{\text{molar volume/cm}^3\,\text{mol}^{-1}}$$

The molar volume of a gas has the value 24 000 cm^3 at room temperature and pressure for all gases.

The two are then compared using the ratio in the equation (see the example of the reaction of magnesium with acid in Section 5.4).

Calculations using solutions

Titration calculations are very common and there are several examples in Sections 5.7 and 5.8. These calculations can be answered using equations such as:

$$\frac{c_A \times V_A}{c_B \times V_B} = \frac{n_A}{n_B}$$

In these calculations, the concentration and volume of solutions A and B and the mole ratio n_A/n_B from the equation are used. In any titration, all but one of the values in this relationship are known and the one unknown is calculated using the results. This formula can be used to analyse titration results, but it is generally better to work out the results step by step, as shown in the worked example in Section 5.8.

If a question involves not only solutions, but also masses or gas volumes, then a step-by-step method using the relationships at the start of Section A1.5 must be used.

Example

What volume of carbon dioxide (at room temperature and pressure) is produced when 50.0 cm^3 of 0.150 mol dm^{-3} hydrochloric acid reacts with excess calcium carbonate?

The molar volume is 24 000 cm^3 at room temperature and pressure.

Notes on the method

Start by writing the equation for the reaction.

Convert the volume and concentration of hydrochloric acid to an amount in moles.

Use the equation to determine the amount of carbon dioxide formed, in moles.

Multiply the amount of gas in moles by the molar volume at room temperature and pressure.

Answer

The equation for the reaction is:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

$$\text{amount of hydrochloric acid} = \frac{50.0}{1000}\,dm^3 \times 0.150\,mol\,dm^{-3} = 7.50 \times 10^{-3}\,mol$$

From the equation, 2 mol hydrochloric acid produce 1 mol carbon dioxide.

$$\therefore \text{amount/mol of carbon dioxide formed} = \tfrac{1}{2}(7.50 \times 10^{-3}) = 3.75 \times 10^{-3}\,mol$$

$$\text{volume of carbon dioxide} = 3.75 \times 10^{-3}\,mol \times 24\,000\,cm^3\,mol^{-1} = 90.0\,cm^3 \text{ (3 s.f.)}$$

Percentage yields and atom economy

The mass or volume of the product calculated in the examples above assumes everything works perfectly. In reality and for several reasons, few reactions produce exactly the mass predicted from the equation, the **theoretical yield**, and instead only a proportion of this mass is formed, the **actual yield** (Section 5.10).

Key terms

The **theoretical yield** is the mass of product obtained if the reaction goes according to the equation.

The **actual yield** is the mass of product obtained from a reaction.

Tip

Don't forget to multiply the M_r of each substance by the number of moles of that substance in the equation when adding all the molar masses together.

Key terms

$$\textbf{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

$$\textbf{Atom economy} = \frac{\text{molar mass of the desired product}}{\text{sum of the molar masses of all the products}} \times 100$$

The ratio of the two is called the **percentage yield**.

Manufacturers continually try to improve the efficiency of their processes to increase the percentage yield of the desired product. However, there is increasing concern about the amount of waste also produced in some processes, even if the percentage yield of the desired product is high.

The overall efficiency of a chemical process is now referred to by the term **atom economy**, which is the molar mass of the desired product expressed as a percentage of the sum of the molar masses of all the products in the equation for the reaction (see the example in Section 5.10).

A1.7 Graphs

Experimental data

Drawing a graph can turn a list of numbers, or numerical data, into a picture which shows if there is a pattern in the results of an experiment. The pattern may be a straight line or a curve, or there may be no pattern. Plotting a graph by drawing a **best-fit line** is a way of averaging results and checking for anomalous results (see the Activity: Finding the formula of red copper oxide, in Section 5.2).

It is also possible to use a mathematical equation to represent the pattern of the graph and so draw mathematical conclusions about the experiment which produced the data (see the Activity: Investigation of the effect of concentration on the rate of a reaction, in Section 9.3). If the graph is a straight line through the origin, then it is possible to say that one **variable** is directly proportional to another variable.

The use of graphs is a very important part of the study of kinetics. For instance, in the study of the reaction between magnesium and hydrochloric acid (Section 9.2), the volume of hydrogen evolved is plotted against time. Time (*x*-axis) is the **independent variable** and the volume of hydrogen (*y*-axis) is the **dependent variable**.

The rate of a reaction at a particular point is given by the gradient of a graph at that point. The gradient is found by drawing a tangent to the graph; the steeper the gradient, the faster the reaction.

The rate of reaction at the start of the experiment, as soon as the reagents are mixed, provides a useful way of studying the effect of changing one variable. Measuring this initial rate is described in Section 9.2.

Sometimes it is useful to extend a graph beyond the range of values measured in the experiment in a process called **extrapolation**. Useful examples of

Tip

When plotting a graph, choose a scale for each axis that allows you to fill as much of the available space as possible, but make sure the scale is simple to use. You do not have to include zero or the origin in all cases. Label each axis of the graph with a quantity divided by its unit, for instance Mass of red copper oxide/g.

Key terms

A **best-fit line** is a smooth line through the middle of the points on a graph.

A **variable** in an experiment is an item, factor, or condition that can be controlled, changed or measured.

The **independent variable** is the one condition that is changed in an experiment.

The **dependent variable** is the variable that is measured; its value depends on the changes made to the independent variable.

Extrapolation of a graph extends the line beyond the experimental range of values.

extrapolation occur in experiments where temperature changes are measured (see the Activity: Measuring and evaluating the enthalpy change for the reaction of zinc with copper(II) sulfate solution, in Section 8.4).

Because of energy losses, the maximum temperature measured is less than it should have been. When the exothermic reaction has ended, the temperature falls back to room temperature at a steady rate. By extending this cooling curve back to the time of mixing, an estimate of what the maximum temperature would have been, had there been no loss of energy to the surroundings, can be obtained for use in the enthalpy change calculation.

Maxwell–Boltzmann distributions and reaction profiles

One of the fundamental models of chemistry is the collision theory. This states that molecules must collide before a reaction can occur and that the molecules which collide must have sufficient activation energy to react.

A Maxwell–Boltzmann distribution shows the spread of molecular kinetic energies for a gas at a particular temperature (Section 9.4). The curve shows that there is a wide spread of molecular energies, meaning that in a sample of gas at a given temperature the molecules do not all have the same energy and so do not all move at the same speed. This variation occurs because molecules collide, and when they do so there is a transfer of energy between them. The distribution plots energy on the *x*-axis against the fraction of molecules with a particular energy on the *y*-axis. Strictly, there is no maximum energy for a molecule, so the *x*-axis should continue to infinity. The area under the curve sums all the fractions of molecules and so represents the total number of molecules.

You should note that these curves are not symmetrical. The peak of a curve, showing the percentage of molecules with the most probable energy, lies to the left of the average energy. The curve starts at the origin – there are no molecules with zero energy. The curve approaches the *x*-axis but never reaches it. There are very few molecules at high energy.

These curves help to explain the effect on the rate of a gaseous reaction of changes in temperature, pressure, concentration and the addition of a catalyst.

Reaction profiles, such as that shown in Figure 9.17 in Section 9.4, are linked to these distributions. These show the progress of a reaction from reactant to product, overcoming activation energy barriers. The *y*-axis shows the energy level at each stage of a reaction, including any intermediates formed. These diagrams give a measure of the activation energy and the overall enthalpy change for a reaction. The *x*-axis is not quantified and is usually simply labelled 'progress of reaction' with no scale.

Mass and infrared spectra

Mass spectra

The information produced in a mass spectrometer can be displayed in two ways, either as a list of the relative abundance of each ion detected, including the molecular ion and each fragment ion, or alternatively as a graphical trace called a mass spectrum (Section 7.1).

A mass spectrum shows all the information from the list but in an easily understood graphical form. The *x*-axis is labelled mass to charge ratio (*m*/*z*) but, since most ions are 1+, $z = 1$ and so the *x*-axis is effectively the relative mass of the ions. The *y*-axis represents the relative abundance of the ions. The tallest peak, the peak for the most abundant ion, is given the relative abundance value of 100% and the abundance of each other ion is measured relative to this peak. The most abundant ion is often *not* the molecular ion, if fragmentation easily occurs.

Tip

There may be peaks with (*m*/*z*) values one or two units greater than the molecular ion. This occurs when isotopes are present. The M+1 peak occurs in organic molecules because about 1% of carbon atoms exist as ^{13}C. If a molecule contains several ^{13}C atoms, then the relative abundance of this ion will become greater. M+2 peaks occur if chlorine or bromine atoms are present.

Infrared spectra

An infrared spectrum (Section 7.2) is obtained by passing infrared radiation through a sample and observing where radiation is absorbed. Absorption corresponds to the natural frequencies at which vibrating bonds in the molecule bend or stretch. The spectrum shows the absorption of energy across a given range of frequencies.

The frequencies of vibrations lie in the infrared region between 1.20×10^{13} and 1.20×10^{14} Hz.

These values correspond to wavelengths between 2.5×10^{-5} and 2.5×10^{-6} m. Rather than use wavelengths with these very small numbers, spectroscopists prefer to work in wavenumbers. The wavenumber is the number of waves in 1 cm, so the range of wavenumbers used is from 400 to 4000 cm^{-1}. The spectra are drawn with the wavenumber values on the *x*-axis increasing from **right** (400 cm^{-1}) to **left** (4000 cm^{-1}) as this shows *increasing* wavelength from left to right.

The *y*-axis is labelled Transmittance/%. If there is no absorption, there is 100% transmittance but, when absorption occurs, there is a dip in transmittance. These dips are still called 'peaks' because they indicate high levels of absorption.

Tip

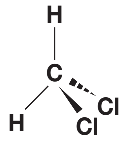
Scanning the range between 4000 cm^{-1} to 400 cm^{-1} in sequence takes a long time. To speed up the process, modern infrared spectrometers pass infrared radiation of several wavenumbers through the sample at the same time. This produces extremely complicated results which are analysed by a mathematical technique called Fourier analysis. This is why modern infrared spectrometers are called 'Fourier transform infrared spectrometers'.

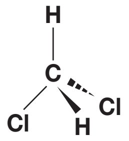
A1.8 Geometry

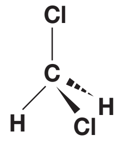
All giant structures are three-dimensional lattices. Apart from some small molecules, molecular compounds are also 3D structures. Chemists need to be able to think in 3D. They also need to be able to represent substances using 3D models or in 2D on flat surfaces such as paper. They should realise, for instance, that the nine structures shown on page 300 all represent the same molecule.

Dichloromethane, CH_2Cl_2, is a tetrahedral molecule and can be represented either in 3D or by 'flat' drawings. In all cases, the structure shown has a central carbon atom surrounded by four bonds located 109.5° apart from each other.

In each of the first three 3D representations, the two normal lines represent covalent bonds in the plane of the paper. The solid wedge represents a bond coming out of the paper, while the hashed bond represents a bond going into the paper.

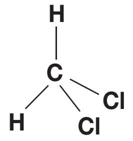


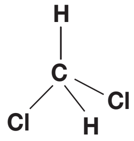


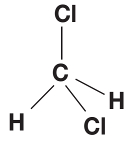


Rotating the structures should demonstrate that they are all the same molecule.

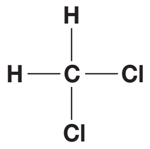
But drawing 3D structures is fairly difficult, so molecules are sometimes represented with normal line or dotted line bonds, but still with an attempt at 3D structures as shown here.

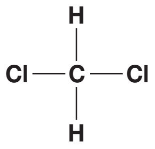


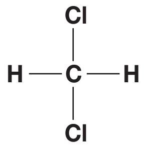




More commonly, molecules are shown as flat structures (as below). In this case, chemists have to remember that the bond angles shown as 90° or 180° are all the tetrahedral angle, 109.5°. Although these look like flat crosses, the four bonds are arranged tetrahedrally around the central carbon atom in exactly the same way as in the six structures above.







The shapes of molecules with a central atom surrounded by between 2 and 6 pairs of electrons are discussed in Section 2.4, together with the effect of the extra repulsion if some of the pairs are lone pairs.

You should learn the five common molecule shapes and try to recognise them whenever they appear.

So, the trigonal planar arrangement of BF_3, with bond angles of 120°, is also seen in the bonding around the carbons in ethene or in a carbocation (Section 6.2.10) or the carbonate ion, CO_3^{2-}.

The tetrahedral arrangement is seen in every alkane but also in the ammonium ion, NH_4^+, and the sulfate ion, SO_4^{2-}.

The trigonal bipyramid structure is seen in the transition state when nucleophilic substitution occurs at a primary halogenoalkane (S_N2) (Chapter 6.3). The bond which is forming, the bond which is breaking, plus the three unchanged bonds are as far apart from each other as possible – the same arrangement as in a molecule of PF_5 – so there are bond angles of 120° and 90° in the structure.

A2 Preparing for the exam

A2.1 Revision

Understanding what you need to know and do

Your revision should be systematic and based on a copy of the Edexcel A Level specification. The specification tells you what you have to know, understand and be able to do. However, the language is very concise and mainly written for teachers. This textbook has been written to cover the specification. The chapters are in the same order as the specification, so, if you are puzzled by a statement in the content, look for guidance in the related chapter in this book.

The specification includes a table showing the assessment objectives for the course. This table may seem rather technical and unimportant, but it will help you to understand what you have to be able to do when answering questions in examinations. There are three assessment objectives: AO1, AO2 and AO3.

In the AS exams at the end of the first part of the Edexcel course, about 35–37% of the marks test your **knowledge and understanding** of the content. This is AO1. There will be questions asking you to show that you can recall facts, patterns and principles. There will also be questions asking you to translate information from one form to another, carry out simple calculations of a kind you have seen before, and to solve problems in familiar contexts.

About 41–43% of the marks test AO2, which covers your ability to **apply** your knowledge and understanding of scientific ideas, processes, techniques and procedures in a range of contexts, which could be familiar or unfamiliar:

- in a theoretical context
- in a practical context
- when handling qualitative data
- when handling quantitative data.

Then about 20–23% of the marks are allocated to AO3, which covers your ability to **analyse, interpret and evaluate** scientific information, ideas and evidence which you have not seen before. This requires you to be able to:

- make judgements and reach conclusions
- develop and refine practical design and procedures.

So, you can see that it is very important that you have the confidence to apply your chemical understanding to unfamiliar situations in which you may have to interpret new sets of data and information, including that presented in tables, charts or graphs. This confidence comes with practice. You need to be able to link together ideas from different fields of chemistry to offer explanations or construct arguments.

Chemistry is a practical subject and high-scoring students not only develop good technical skills in the laboratory, but also develop a strategic sense of the ways that experiments are planned and carried out to give meaningful results. Examination questions will ask you to describe how experiments were carried out and what happened; they will also ask you to explain the rationale for the procedures. You will also be asked to interpret the results of experiments qualitatively and quantitatively, and to draw valid conclusions from data, taking into account measurement uncertainty.

Tip

See the Practical skills sheets, accessed via the QR codes on pages 312 and 313, for more guidance on practical procedures, measurements and the evaluation of experimental data.

Understanding the course as a whole

Some questions in the examinations expect you to bring together your knowledge and understanding of different areas of chemistry, applying them in contexts that may be new to you. This is sometimes called synoptic assessment. The term 'synoptic' implies that you have an understanding of the course as a whole, and an appreciation of how the different topics in the course hang together and relate to each other.

So, any synoptic questions require you to work across different parts of the specification and to show that you can draw on ideas and information from different topics to answer questions or solve problems.

Revision notes

Check that you have your own notes on all sections of the specification. Organise your notes with clear titles and subheadings. Highlight key points in colour. Include mnemonics if you find them helpful, such as:

- OIL RIG (oxidation is loss, reduction is gain
- MEPrB (methane, ethane, propane, butane)
- ALSUB (axes, labels, scales, units, points).

Flow diagrams can be helpful in giving you an overview of organic chemistry.

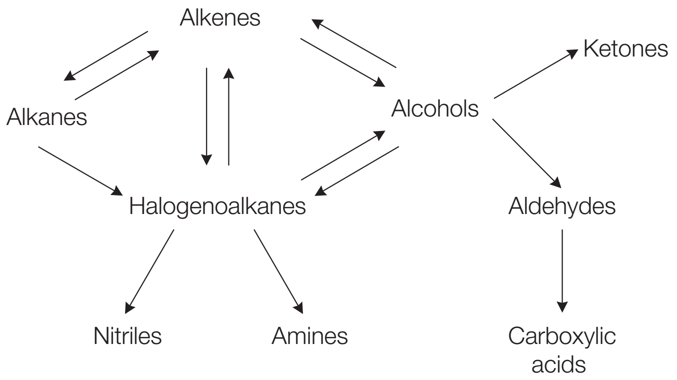


Figure A2.1 Relationships between series of organic compounds. Make a copy of the diagram, then add examples with formulae and label the arrows to show how one functional group can be converted to another.

Active revision

You need to make your revision active, so that you maintain concentration and really test that you understand the key points, while developing the necessary skills. For each revision topic, try writing the title of a topic in the centre of a sheet of paper. Then use the definitions and explanations in the main part of this book to help you build up a mind map or concept map to show how the ideas in the topic link together.

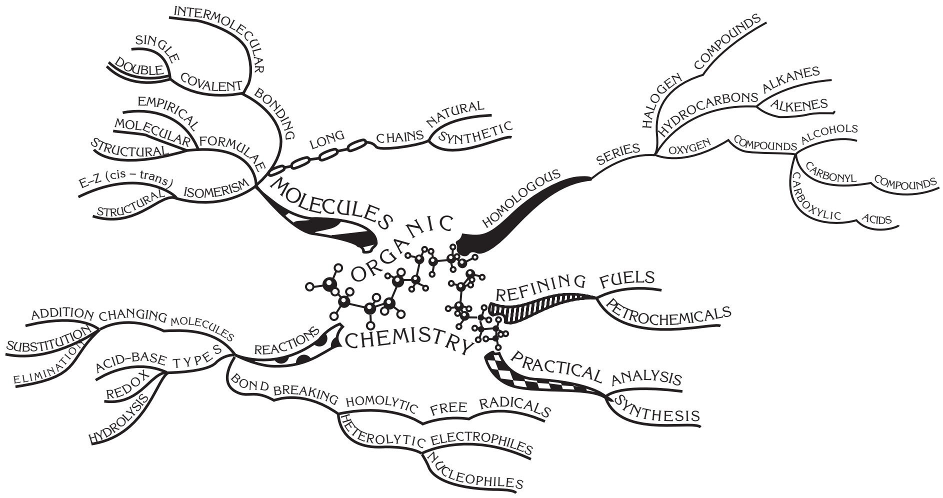

ORGANIC CHEMISTRY
MOLECULES
INTERMOLECULAR
SINGLE
DOUBLE
COVALENT
BONDING
EMPIRICAL
MOLECULAR
STRUCTURAL
FORMULAE
E-Z (cis – trans)
STRUCTURAL
ISOMERISM
LONG
CHAINS
NATURAL
SYNTHETIC
HOMOLOGOUS
SERIES
HALOGEN
COMPOUNDS
HYDROCARBONS
ALKANES
ALKENES
OXYGEN
COMPOUNDS
ALCOHOLS
CARBONYL
COMPOUNDS
CARBOXYLIC
ACIDS
REFINING
FUELS
PETROCHEMICALS
PRACTICAL
ANALYSIS
SYNTHESIS
REACTIONS
CHANGING MOLECULES
ADDITION
SUBSTITUTION
ELIMINATION
TYPES
ACID–BASE
REDOX
HYDROLYSIS
BOND BREAKING
HOMOLYTIC
FREE RADICALS
HETEROLYTIC
ELECTROPHILES
NUCLEOPHILES

Figure A2.2 The start of a mind map for introductory organic chemistry.

Suppose you are revising the chemistry of the halogens. Have a pile of scrap paper to hand and a pencil. Now, as you read, make jottings, small lists, summary phrases, write equations, sketch diagrams and practise labelling them. Now tear up the paper, close the textbooks and notes, and write out those lists, equations, diagrams and so on. Then check to see whether you have remembered correctly.

Tip

Learn key definitions thoroughly. Even top candidates frequently lose marks by missing out key words when asked to state what is meant by chemical terms. Use the online glossary to help you.

When it comes to learning the reactions of a family of organic compounds such as the alcohols, consider using a set of cards. Write the equation for each alcohol reaction you have to know on one side of the card. Write the names of the reactants and the conditions for the reaction on the other side. Now you can use the cards for revision. Look at one side of the card and try to recall what is on the other side. Similarly, test yourself using the expanded glossary available online with this textbook.

Practise calculations with the help of worked examples. Even if you have answered all the 'Test yourself' questions in this book, it is worth working through them again, including the calculations, checking your responses with the answers provided online.

One of the key characteristics of a high-scoring candidate is the ability to carry out complex calculations, setting out the working step by step and including the correct symbols and units. The worked examples in this textbook show you how to do this. Among the important calculations are those to work out titration results and thermochemistry calculations.

A2.2 Exam technique

Past papers, mark schemes and examiners' reports

Look at past papers and practise answering the questions. Some topics in the specification are so important that they are tested in most years with only very minor differences in emphasis and phrasing of questions. It is because so many questions on some topics appear to be the similar year after year, that you must read the questions with the greatest of care to note the particular emphasis, and the precise nature of a question.

Looking at some past mark schemes can be helpful, but you need to bear in mind that they are mainly intended to help examiners give marks accurately, so they are presented very concisely and do not include full answers. However, the mark schemes for longer questions will show you what examiners are looking for when there are 3–6 marks for part of a question.

For some questions examiners expect you to write at greater length, drawing together and organising relevant material. No marks are allocated for the plan you sketch out before writing your answer, but making a plan helps you to write a well organised answer with examples and so leads to better marks.

Examiners' reports have traditionally been written for teachers, but increasingly they include information that students find helpful. You can download the reports from the Edexcel website. You will find that the report on a particular examination paper includes sample answers from students, together with comments and tips from the examiners. Working through some of these reports will show you how to answer questions in the ways that gain most marks, and how to avoid common errors.

One of the most useful revision activities is to answer the questions in past examination papers and then to check your answers against the published mark scheme.

Question types

The Edexcel examination papers consist of a series of structured questions. Each question is set in a particular chemical context. If the context is familiar, it may just be introduced by a short sentence, such as: 'This question is about Group 2 and enthalpy changes.' However, there are other questions which start with much more information and data. For example, there might be a summary of the procedure for an experiment, followed by some sample results. Examiners do not include information that you do not need. It is essential that you read the *introduction* to a question very carefully because you need it to answer the parts of the question.

Sometimes the introductory information at the start of a question will seem strange. This is not because the examiner has made a mistake or your teacher has failed to cover some part of the specification. As shown by the assessment objectives, the skills being tested in the examinations include your ability to apply your knowledge to *unfamiliar* situations. You can be confident that the examiner has chosen a context and given data that you can be expected to make sense of using the chemistry that you have learned during the course.

Within the structured questions there are three main question types: multiple-choice questions, short-answer questions and questions asking for a longer answer.

Multiple-choice questions

Multiple-choice questions can seem deceptively simple, because you are given four choices and have to choose one of them. Sometimes they test your knowledge of a basic idea and, if you know the answer, you will be able to answer the question quickly. However, some questions require careful thinking and may involve a calculation.

If a multiple-choice question involves a calculation you should not try to do it in your head. Write down your working in rough using a blank part of the question paper.

As always, you need to read the questions carefully, especially if the words 'not' or 'never' are included in the working. A questions which includes 'not' can be confusing as in: 'Which substance is **not** a product of the incomplete combustion of hexane?'. You have to pick the one of the four options that is **not** produced in the reaction.

You do not lose marks if you make the wrong choice, so you should always answer every multiple-choice question. Sometimes you may be able to reject two of the options as wrong, but then find that you are not sure which of the remaining two options is correct. You should make an intelligent guess and pick one of them.

Short-answer questions

Most of the parts of a structured question demand short answers worth 1–3 marks. Typical parts of such questions involve:

- naming, stating or giving information
- writing balanced equations
- describing reactions
- explaining the meaning of key terms
- plotting graphs
- interpreting data
- performing calculations.

When answering these questions, you should use the space allowed for your answer and the number of marks allocated to guide you when deciding how much to write. Three marks for part of a question probably means that the examiner is expecting three good points to be made. If asked for a chemical test, for example, one mark might be for the reagent to be used, one for the conditions and the third for describing the observations.

As explained in the next section, it is very important that you pay attention to the 'command words' and provide the type of answer that the examiner has asked for.

Tip

In an examination, aim to gain maximum marks for minimum knowledge.

- Score marks in all questions.
- Never leave a question blank because you are short of time.
- It is much easier to score the first few marks in a question than the last few marks.
- Answer the question asked.
- Make sure you don't leave any parts out.
- There are no marks for unnecessary extra information.

Tip

Watch your language. Don't use the wrong words.

- Do you mean ions or atoms or molecules?
  Don't use the words 'atom' or 'molecule' when discussing an ionic lattice such as sodium chloride.
  Don't use the word chlor**ide** (for the ion) when you mean atoms or molecules of the element chlor**ine** (and vice versa).
- Bonds or forces?
  Molecules have covalent bonds between atoms within/inside the molecules. These do **not** break when molecular substances melt or boil.
  Between the molecules there are (intermolecular) forces, not bonds.
  These forces are overcome when a molecular substances melt or boils

Longer answer questions

Questions requiring longer answers carry 4–6 marks in the Edexcel examination papers. Some of them ask for a description, interpretation or explanation; others require a calculation that involves several stages. Here, too, you must pay careful attention to the command words.

In a prose answer, you will not get credit for copying phrases from the question. This seems obvious but students commonly lose marks by simply repeating the question. It can help to jot down key points in rough so that you can decide on the best order to cover them. Write short, clear sentences. Keep your answer relevant by dealing with all the points asked for in the question.

If you are asked to carry out an extended calculation, without any help from the structure of the question, you must set out your working step by step with enough words to show what you are doing at each step. The worked examples in the main chapters of this textbook show you how to do this for each of the types of calculation that feature in this course. Marks are awarded for each stage of the quantitative argument, as you can see by looking at Edexcel mark schemes.

Examiners' terms

Every year, too many well-prepared candidates fail to score as many marks as they should because they do not answer the question set by the examiners.

Examiners try very hard to set questions which are clear to candidates. Even so, under examination conditions, it is all too easy to rush into writing an answer before checking carefully what you have been asked to do by the examiner. You do not get marks if you fail to answer the question that the examiner has set you.

A useful first step is to highlight the command words in the question. Words such as 'calculate', 'describe' and 'explain' give instructions.

The command words used by examiners in Edexcel chemistry papers are defined in Appendix 7 of the specification.

Tip

Curly arrows in organic mechanisms must start at a bond or a lone pair and end forming a new bond or a lone pair on an atom. Don't forget to add the dipoles to relevant bonds too.

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Note: page numbers in **bold** refer to illustrations.

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6.3 Halogenoalkanes and alcohols

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8 Energetics I

9 Kinetics I

10 Equilibrium I

Preparing for practical assessment

The periodic table of elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0(8)
(1)	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*	*(13)*	*(14)*	*(15)*	*(16)*	*(17)*	*(18)*
							1.0 **H** hydrogen 1										4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12											27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac**** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** damstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112–116 have been reported but not fully authenticated

*Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
**Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103